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THERMODYNAMIC PROPERTIES OF *cis*-2-BUTENE FROM 15° TO 1,500°K[1]

By Russell B. Scott, W. Julian Ferguson, and Ferdinand G. Brickwedde

ABSTRACT

The following properties of a sample of *cis*–2–butene, 99.94 percent pure, were measured: (1) the specific heat of solid and of liquid from 15° to 300°K, (2) heat of fusion at the triple point (130.25 int. joule g^{-1}), (3) triple-point temperature (-138.900 ± 0.008° C), (4) heats of vaporization at several temperatures between 246° and 293°K, and (5) vapor pressure from 200° to 296°K. With these experimental data, calculations were made of (1) the normal boiling temperature (3.718°C), (2) volume of the saturated vapor, (3) enthalpy and entropy of the solid and the liquid from 0° to 300°K, and (4) entropy, enthalpy, and specific heat of the vapor in the ideal gas state from 245° to 300°K. Thermodynamic functions for *cis*–2–butene in the ideal gas state from 300° to 1,500°K were calculated from spectroscopic data. Thermodynamic data for the *cis-trans* isomerization of 2–butene are included.

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I. INTRODUCTION

The measurements and calculations described in this paper constitute a continuation of the program of obtaining data on the properties of materials that are of interest in the chemistry of synthetic rubber.

[1] The investigation reported in this paper is part of a joint program with the Cryogenic Laboratory, The Pennsylvania State College, on the C_4 hydrocarbons.

The properties measured include the specific heat at saturation pressure of solid and of liquid *cis*-2-butene from 15° to 300° K, heat of fusion, heat of vaporization at several temperatures between 246° and 292° K, and vapor pressure over the temperature range 200° to 296° K. These experimental data were used to calculate: (1) the volume of the saturated vapor, (2) enthalpy and entropy of the solid and the liquid from 0° to 300° K, and (3) enthalpy, entropy, and specific heat of the vapor in the ideal gas state from 245° to 300° K.

A frequency assignment for the internal vibrations of *cis*-2-butene based upon the infrared absorption and Raman spectra reported by Gershinowitz and Wilson [10],[2] was used to calculate the barrier restricting internal rotation of the methyl groups from the gaseous specific heat data of Kistiakowsky and Rice [9]. The spectroscopic value for the entropy of *cis*-butene in the ideal gas state involving this barrier is in good agreement with the experimental value of the entropy determined from the calorimetric data. From this frequency assignment and value for the barrier, tables were computed for the thermodynamic functions of *cis*-2-butene in the ideal gas state from 300° to 1,500° K.

II. MATERIAL

The *cis*-2-butene used for these measurements was prepared in a pure state by M. R. Fenske, of The Pennsylvania State College, and was further purified at the Bureau by two fractional crystallizations, in which about one-third of the original sample of 122 g was discarded. A volatile impurity, which may have been air, was removed by condensing the material into a trap surrounded by liquid air while maintaining a high vacuum on the trap. Sixty-four grams of the material thus purified was used in the calorimetric investigations. The amount of impurity in this sample, assuming the impurity to be insoluble in solid *cis*-butene, was computed from measurements taken with the calorimeter, which gave the melting temperature as a function of the fraction melted. The temperature at which 50 percent of the sample was melted was found to be 0.0116° K lower than the temperature at which 99+ percent was melted. This corresponds to a "liquid soluble, solid insoluble" impurity of 0.057 mole percent.

III. APPARATUS

This investigation was carried out with the same apparatus used for the measurements on 1,3-butadiene. The calorimeter was similar to the adiabatic vacuum type of Southard and Brickwedde [1], but was modified somewhat for the measurement of heats of vaporization and to improve the temperature distribution and for ease of control. A manuscript on 1,3-butadiene [2], giving a complete description of the apparatus, methods of measurement, and correlation of the data, has been prepared.

IV. SPECIFIC HEAT

The data from which the specific heats were calculated were obtained in two sets of measurements of the heat capacity of the calorimeter and contents, first with a large amount of material in the calorimeter

[2] Figures in brackets indicate the literature references at the end of this paper.

and then with a small amount. If G_b is the heat capacity of the calorimeter plus an amount of material M_b, and G_a is the heat capacity of the calorimeter plus an amount of material M_a, then the specific heat of the material in the condensed state at saturation pressure is

$$C_{sat.}=\frac{G_b-G_a}{M_b-M_a}+T\frac{d}{dT}\left(v\frac{dP}{dT}\right),^{3} \tag{1}$$

where T is the absolute temperature, v is the specific volume of the condensed phase, and P is the vapor pressure. This relation was derived from equation 11 of the paper by N. S. Osborne [3]. The first term of the right-hand member of equation 1 would be the specific heat if the substance were not volatile. The last term of this equation takes account of the heat required to vaporize some of the material during a heat-capacity determination so as to maintain saturation vapor pressure. In the present experiment, the large mass, M_b, consisted of 64.235 g of *cis*-2-butene, and the small mass, M_a, was 0.740 g.

The values of v, the specific volume of the liquid, were obtained from a table compiled by Cragoe [4]. Values of dP/dT were obtained from vapor-pressure equation 5, p. 7. At temperatures below 85°K no measurements were made with the small amount of material in the calorimeter, G_a being taken as the heat capacity of the completely empty calorimeter, as determined by earlier measurements, M_a being zero of course. This was permissible, since below 165° K the last term in equation 1 is negligible. At temperatures between 85° and 130° K, inclusive, the specific heats were calculated by both methods, first from the values of G_a and M_a obtained in this investigation, and then with the earlier values of G_a for the empty calorimeter and the value zero for M_a. This was done as a check on the reproducibility of the measurements. The maximum difference between the two sets of values for the specific heats in this temperature region was about 1 part in 1,200, and the mean deviation was 1 part in 2,500. The values reported here were obtained by averaging the two sets of values.

Figure 1 gives the specific heat of *cis*-2-butene, and the second column of table 1 gives the results of the specific heat-determinations tabulated at 5-degree intervals. The values at 5° and 10° K were calculated by using the equation

$$C_{sat.}=0.7381\mathrm{D}\left(\frac{150}{T}\right),$$

where D is the Debye specific-heat function. The numerical constants were chosen to fit the data at 15°, 20°, and 25° K.

[3] This relation was derived by Harold J. Hoge.

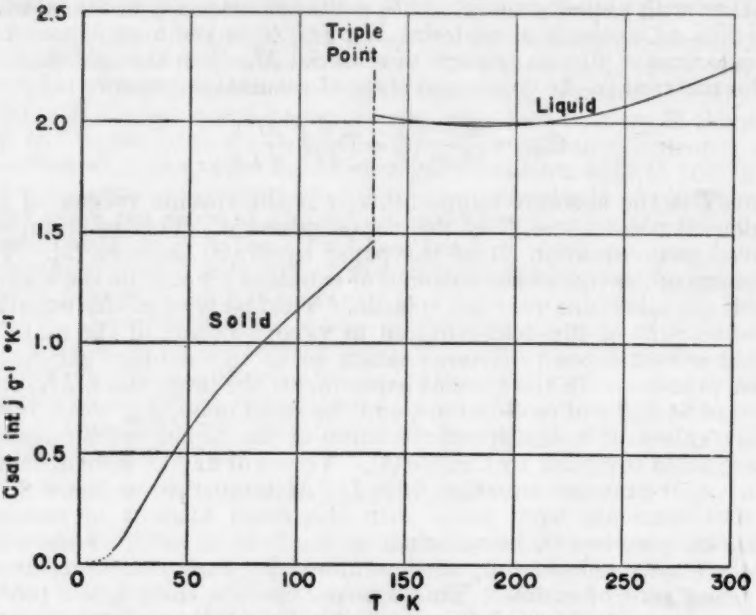

FIGURE 1.—*Specific heat of solid and liquid cis-2-butene.*

TABLE 1.—*Specific heat, entropy, and enthalpy[a] of solid and of liquid cis-2-butene at saturation pressure*

[13.4114 cal mole⁻¹=1 int. j g⁻¹. Atomic weights: C=12.010, H=1.008]

T	$C_{sat.}$	$S_{sat.}$	$\int_0^T C_{sat.}\,dT$	$\int_0^T V_{sat.}\frac{dP}{dt}\,dt$	$(H_{sat.}-E_0^\circ)$
			SOLID		
°K	*Int. j g⁻¹ °K⁻¹*	*Int. j g⁻¹ °K⁻¹*	*Int. j g⁻¹*	*Int. j g⁻¹*	*Int. j g⁻¹*
0	0	0	0	0	0
5	[b].00213	.0007	.0027	----------	.0027
10	[b].01703	.0057	.0426	----------	.0426
15	.05645	.0190	.214	----------	.214
20	.1197	.0435	.648	----------	.648
25	.1969	.0783	1.434	----------	1.434
30	.2812	.1216	2.629	----------	2.629
35	.3669	.1714	4.248	----------	4.248
40	.4496	.2258	6.291	----------	6.291
45	.5280	.2834	8.737	----------	8.737
50	.6012	.3428	11.562	----------	11.562
55	.6705	.4034	14.743	----------	14.743
60	.7370	.4646	18.264	----------	18.264
65	.7979	.5261	22.103	----------	22.103
70	.8551	.5873	26.237	----------	26.237
75	.9091	.6482	30.649	----------	30.649
80	.9602	.7085	35.323	----------	35.323
85	1.0102	.7682	40.249	----------	40.249
90	1.0584	.8273	45.422	----------	45.422
95	1.1040	.8858	50.829	----------	50.829
100	1.1482	.9435	56.460	----------	56.460
105	1.1916	1.0006	62.310	----------	62.310
110	1.2349	1.0570	68.376	----------	68.376
115	1.2790	1.1129	74.660	----------	74.660
120	1.3237	1.1682	81.166	----------	81.166
125	1.3694	1.2232	87.899	----------	87.899
130	1.4164	1.2778	94.863	----------	94.863
134.26	1.4584	1.3242	100.99	----------	100.99

See notes at end of table.

TABLE 1.—*Specific heat, entropy, and enthalpy[a] of solid and of liquid cis-2-butene at saturation pressure*—Continued

T	$C_{sat.}$	$S_{sat.}$	$\int_0^T C_{sat.}dT$	$\int_0^T V_{sat.}\frac{dP}{dt}dt$	$(H_{sat.}-E_0^\circ)$
			LIQUID		
°K	*Int. j g⁻¹ °K⁻¹*	*Int. j g⁻¹ °K⁻¹*	*Int. j g⁻¹*	*Int. j g⁻¹*	*Int. j g⁻¹*
134.26	2.0334	2.2944	231.24	----------	231.24
135	2.0318	2.3055	232.75	----------	232.75
140	2.0209	2.3792	242.88	----------	242.88
145	2.0114	2.4500	252.96	----------	252.96
150	2.0035	2.5180	263.00	----------	263.00
155	1.9974	2.5836	273.00	----------	273.00
160	1.9923	2.6470	282.97	----------	282.97
165	1.9876	2.7082	292.92	----------	292.92
170	1.9840	2.7675	302.85	----------	302.85
175	1.9823	2.8249	312.76	----------	312.76
180	1.9801	2.8808	322.67	----------	322.67
185	1.9803	2.9350	332.57	----------	332.57
190	1.9817	2.9878	342.47	----------	342.47
195	1.9840	3.0393	352.39	----------	352.39
200	1.9867	3.0896	362.31	----------	362.31
205	1.9903	3.1387	372.26	----------	372.26
210	1.9950	3.1867	382.22	0.01	382.23
215	2.0009	3.2337	392.21	.01	392.22
220	2.0081	3.2798	402.23	.01	402.24
225	2.0166	3.3250	412.29	.02	412.31
230	2.0264	3.3695	422.40	.02	422.42
235	2.0372	3.4132	432.56	.03	432.59
240	2.0484	3.4562	442.77	.04	442.81
245	2.0602	3.4985	453.04	.05	453.09
250	2.0731	3.5403	463.38	.06	463.44
255	2.0871	3.5814	473.77	.07	473.85
260	2.1018	3.6221	484.25	.09	484.34
265	2.1178	3.6623	494.79	.11	494.91
270	2.1348	3.7020	505.43	.13	505.56
275	2.1529	3.7414	516.14	.16	516.30
280	2.1716	3.7803	526.96	.19	527.15
285	2.1912	3.8190	537.86	.22	538.08
290	2.2119	3.8572	548.87	.26	549.13
295	2.2335	3.8952	559.98	.30	560.28
298.16[c]	*2.2480*	*3.9191*	*567.08*	*.33*	*567.41*
300	2.2564	3.9330	571.21	.35	571.56

[a] The enthalpy is referred to $H_0^\circ=E_0^\circ$, the internal energy of solid *cis*-butene at 0°K.

[b] Extrapolated, using Debye function, 0.7381D (150/*T*).

[c] =25°C.

V. HEAT OF FUSION AND TRIPLE-POINT TEMPERATURE

The heat of fusion was determined by measuring the amount of electric energy required to heat the calorimeter and contents from a temperature, T_1, below the triple point to a temperature, T_2, above the triple point. If this measured energy is Q_i, then the heat, Q_f, required to melt the contents is

$$Q_f=Q_i-\int_{T_1}^{T_f} G_s dT-\int_{T_f}^{T_2} G_l dT, \qquad (2)$$

where T_f is the triple-point temperature, G_s is the heat capacity of the calorimeter and contents below the triple point, and G_l is the heat

capacity of the calorimeter and contents above the triple point. Two determinations were made, the data and results of which are given in table 2. The mean value of these determinations is 130.25 int. j g^{-1}. The triple-point temperature of the sample used was 134.248°K. As mentioned in section II, measurements were made which gave the solid-liquid equilibrium temperature as a function of the fraction melted. By the use of this function, the triple-point temperature of pure *cis*-2-butene was found to be 134.260°K, or −138.900°C. Although the error arising from this operation is small, an uncertainty of ±0.008° should be assigned to these values of temperature, because differences this large are sometimes found between the scales of standardized platinum resistance thermometers when they are compared at this temperature [17].

TABLE 2.—*Heat of fusion of cis-2-butene*

[13.4114 cal mole $^{-1}$=1 int. j g^{-1}. Atomic weights: C=12.010, H=1.008]

Run	T_1	T_2	Q_T	$\int_{T_1}^{T_f} C_s dT$	$\int_{T_f}^{T_2} C_l dT$	Q_f	$L_f = Q_f/M$ (M=64.235 g)
	°K	°K	*Int. j*	*Int. j*	*Int. j*	*Int. j*	*Int. j* g^{-1}
1	128.00	136.59	9858.4	1019.4	474.2	8364.8	130.22
2	117.69	136.26	11404.0	2626.0	408.6	8369.4	130.29

VI. HEAT OF VAPORIZATION

The heat of vaporization was determined by measuring the electric power required to keep the temperature of the calorimeter constant while withdrawing vapor from the calorimeter at an almost constant rate. The amount of vapor withdrawn during a measured interval of time was determined by allowing the vapor to condense into a weighing flask cooled with solid CO_2 and weighing the flask before and after each run. The rate of withdrawal of vapor varied from 16 to 20 g per hour for the different runs. Previous experience with the calorimeter in measuring the heat of vaporization of 1,3-butadiene had shown that the values obtained for the heat of vaporization were independent of the rate of withdrawal of vapor. The above rate was chosen because the necessary energy input could be conveniently measured with it, and the material withdrawn during a run of from 40 to 60 minutes could be accurately weighed.

The heat of vaporization, L_v, was calculated from the experimental data by means of the relation

$$L_v = \frac{Q}{M}\left(1 - \frac{v}{V}\right), \tag{3}$$

where Q is the amount of electric energy required to keep the temperature of the calorimeter constant while a mass, M, of vapor was withdrawn, v is the specific volume of the liquid, and V is the specific volume of the vapor. If all the vapor produced were withdrawn from the calorimeter and included in the mass, M, Q/M would be the heat of vaporization. However, some of the vapor produced does not leave the calorimeter but fills the space vacated by the evaporated liquid. This is accounted for by the factor $(1-\frac{v}{V})$. Values of v, the specific

volume of the liquid, were obtained from a table by Cragoe [4], and values of V, the specific volume of the vapor, were determined from the equation of state (section VIII) and the vapor-pressure equation (section VII).

In table 3 the results of the measurements of the heat of vaporization are given. It was found that the heat of vaporization as a function of temperature could be represented by the following equation, the constants of which were obtained by the method of least squares:

$$L_v \text{ (int. j g}^{-1}) = 542.53 + 0.07217T - 0.0019098T^2, \quad (4)$$

where T is in degrees Kelvin. The *maximum* deviation of the seven observed results from values obtained from the equation is 0.13 percent and the *average deviation* is 0.08 percent.

TABLE 3.—*Heat of vaporization of cis-2-butene*

[13.4114 cal mole^{-1} =1 int. j g^{-1}. Atomic weights: C=12.010, H=1.008]

T	Q/M	$1-(v/V)$	L_v
°K	*Int. j g*$^{-1}$		*Int. j g*$^{-1}$
246.18	444.47	0.99892	443.99
252.43	440.15	.99854	439.51
252.44	440.18	.99854	439.54
263.29	429.08	.99766	428.97
272.36	421.51	.99663	420.09
279.70	415.32	.99556	413.48
292.25	403.33	.99311	400.55

VII. VAPOR PRESSURE

The vapor pressures of a sample of cis-2-butene in the calorimeter were measured with a mercury manometer connected to the calorimeter for this purpose. The heights of the mercury columns were read on a mirror-backed glass scale, having 1-mm divisions, supported in contact with the manometer tubes. For pressures below 1 atmosphere, one arm of the manometer was evacuated. For pressures between 1 and 2 atmospheres this manometer arm was open to the atmosphere, atmospheric pressure being measured with a precision barometer. The inside diameter of the manometer tubes was 10 mm. The readings were corrected for capillary depression due to different meniscus heights and reduced to standard conditions (0°C and g=980.665 cm sec^{-2}). The heights were read to 0.1 mm Hg, although hundredths millimeter were carried after averaging and computing the corrections.

The results of the vapor pressure measurements are given in table 4. It was found that the observed data could be represented within the accuracy of measurement by the equation

$$\log_{10}P = 12.64318 - \frac{1808.945}{T} - 0.0162822T + 1.6686\times10^{-5}T^2, \quad (5)$$

in which the pressures are expressed in millimeters of mercury at standard conditions (0° C and g=980.665 cm sec^{-2}), and where T, the Kelvin temperature, is equal to 273.160°+t° C. Values of vapor pressure computed from this equation are given in column 3 of table 4, and the differences between the observed and calculated pressures are given in column 4. The normal boiling point of cis-2-butene, obtained

by setting P equal to 760 mm Hg in equation 5, is 276.878° K, or 3.718° C. From Raoult's law a nonvolatile impurity of 0.057 mole percent (sec. II) corresponds to an error of 0.016° C in boiling point.

TABLE 4.—*Vapor pressure of cis-2-butene in millimeters of mercury at standard conditions*

[0° C and g=980.665 cm sec^{-2}]

T[1]	$P_{obs.}$	$P_{calc.}$	ΔP obs.−calc.	T[1]	$P_{obs.}$	$P_{calc.}$	ΔP obs.−calc.
°K	mm Hg	mm Hg	mm Hg	°K	mm Hg	mm Hg	mm Hg
203.070	13.09	13.09	0.00	266.454	501.51	501.68	−.17
210.612	23.15	23.18	−.03	273.720	672.53	672.73	−.20
217.790	38.29	38.25	+.04	276.849	759.14	759.15	−.01
225.057	61.12	61.12	.00	279.862	850.50	850.35	+.15
233.085	98.58	98.55	+.03	284.304	1000.27	1000.19	+.08
241.613	157.18	157.15	+.03	288.680	1167.07	1167.13	−.06
250.031	240.04	240.09	−.05	293.045	1354.53	1354.38	+.15
258.338	353.25	353.37	−.12	295.919	1489.85	1489.91	−.06
266.444	501.46	501.48	−.02				

[1] T °K=273.160°+t °C.

VIII. PROPERTIES DERIVABLE FROM THE CALORIMETRIC AND VAPOR-PRESSURE DATA

1. ENTROPY AND ENTHALPY OF SOLID AND OF LIQUID

In table 1, column 3, values of the entropy, $S_{sat.}$, of *cis*-2-butene in the solid and the liquid states at saturation pressure are given at 5-degree intervals. These were obtained by a tabular integration of values of $C_{sat.}/T$ by means of Simpson's rule. Values $(H_{sat.}-E_0^*)$ of the enthalpy of the condensed phases at saturation pressure relative to the internal energy, E_0^*, of solid *cis*-butene at 0°K are given in column 6, table 1. These were obtained from the following relations:

$$H_{sat.}-E_0^*=\int_0^T C_{sat.}dT+\int_0^T v_{sat.}\left(\frac{dP}{dT}\right)_{sat.}dT \tag{6a}$$

for the solid, and

$$H_{sat.}-E_0^*=\int_0^T C_{sat.}dT+\int_0^T v_{sat.}\left(\frac{dP}{dT}\right)_{sat.}dT+L_f \tag{6b}$$

for the liquid, where $v_{sat.}$ is the specific volume of the condensed phase in equilibrium with vapor, P is the vapor pressure, and L_f is the heat of fusion. The integrals were evaluated by the tabular method mentioned above. Values of dP/dT were obtained by differentiating the vapor-pressure equation 5, and values of $v_{sat.}$ were taken from the table by Cragoe [4].

The integrations were checked by performing the additional integration $\int_0^T S_{sat.}dT$ and also obtaining values of $TS_{sat.}$. Since

$$\int_0^T S_{sat.}dT=TS_{sat.}-\int_0^T C_{sat.}dT-L_f, \tag{7}$$

an error in the integrations involved in the calculations of $H_{sat.}$ will appear when comparing the values obtained for the two sides of this equation.

2. SPECIFIC VOLUME OF THE VAPOR

The heat of vaporization and vapor-pressure data were used to compute the specific volume of the saturated vapor by means of the Clausius-Clapeyron relation.

$$V-v=\frac{L_v}{T\left(\frac{dP}{dT}\right)_{sat.}}, \tag{8}$$

where V and v are the volumes of the saturated vapor and liquid, respectively, L_v is the observed heat of vaporization (table 3), T is the Kelvin temperature, and $(dP/dT)_{sat.}$ is the temperature derivative of the vapor-pressure equation, 5. Values of V thus obtained are given in table 5.

TABLE 5.—*Volumes of saturated cis-2-butene vapor derived from calorimetric and vapor-pressure data*

T[1]	P (saturation pressure)	V	PV/RT
°K	*mm* Hg	*ml* g^{-1}	
246.18	198.62	1359.7	0.9869
252.43	269.26	1027.6	.9862
252.44	269.40	1027.3	.9863
263.29	438.95	651.69	.9775
272.36	637.66	459.92	.9687
279.70	845.24	353.85	.9620
292.25	1318.7	232.74	.9448

[1] T °K=273.16°+t °C.

If an equation of state of the form

$$\frac{pV}{RT}=1-\frac{k}{VT^2} \tag{9}$$

is assumed, values of k may be obtained from the experimental values of p, V, and T. Thus

$$k=VT^2\left(1-\frac{pV}{RT}\right). \tag{10}$$

Figure 2 shows the values of k obtained in this way. Also included in figure 2 are values of k computed from the direct measurements of volume made by Roper [5]. There are rather large differences at low temperatures between the values of k calculated from our calorimetric and vapor-pressure data and the values of k calculated from Roper's measurements, but the agreement at higher temperatures is good. The disagreement at low temperatures is perhaps not surprising, since the pressures are so low (limited by the vapor pressure) that pV/RT is nearly equal to 1. The value 1.075×10^6 ml g^{-1} °K^2 was selected for k. We think that ±10 percent is a reasonable probable error for this value.

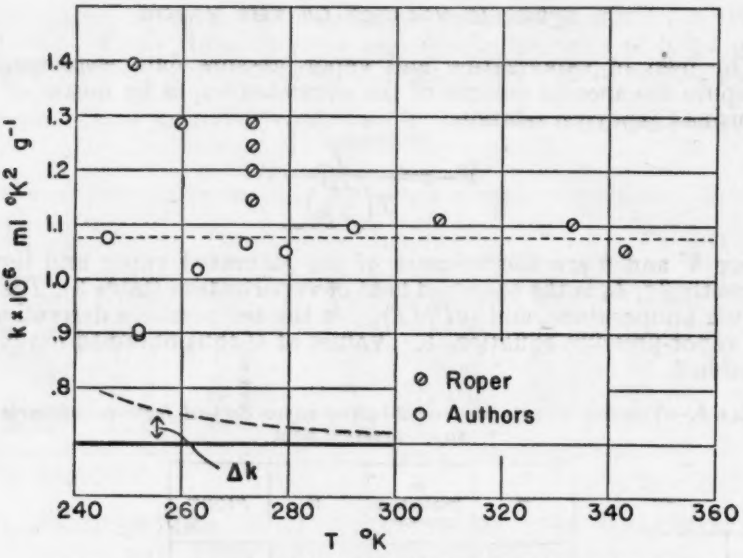

FIGURE 2.—*Experimental values of k in the equation of state, eq 9.*

The horizontal dotted line at $k=1.075\times10^6$ ml °K² g⁻¹ represents the value of k chosen in this investigation. The interval, Δk, bounded by the dotted curve and the horizontal line near the bottom of the graph, represents the error in k that would result from an error of 1 part in 1,000 in $V_{sat.}$, the specific volume of the saturated vapor.

3. THERMAL PROPERTIES OF THE VAPOR

The results thus far obtained were used to compute the enthalpy, entropy, and specific heat at constant pressure of *cis*-2-butene in the ideal gas state. The differences between the enthalpy or entropy of the ideal gas at a pressure of 1 atmosphere and the enthalpy or entropy of the real gas at saturation pressure were obtained from the equation of state, 9, and the thermodynamic relations:

$$\left(\frac{\partial H}{\partial V}\right)_T=T\left(\frac{\partial p}{\partial T}\right)_V+V\left(\frac{\partial p}{\partial V}\right)_T \tag{11}$$

and

$$\left(\frac{\partial S}{\partial V}\right)_T=\left(\frac{\partial p}{\partial T}\right)_V, \tag{12}$$

where H is the enthalpy, V is the volume, T is the absolute temperature, p is the pressure, and S is the entropy. The difference between the enthalpy of the ideal gas and that of the saturated vapor in int. j g^{-1} is

$$H^\circ-H_{sat.}=\frac{3kR}{V_{sat.}}T,$$

where k has the value of 1.075×10^6 ml g^{-1} °K², R is the gas constant for butene in int. j g^{-1} °K^{-1} (0.148168), $V_{sat.}$ is the volume of the saturated vapor in ml g^{-1}, and T is the temperature in degrees kelvin.

The difference between the entropy of the ideal gas at 1 atmosphere and that of the real gas at saturation pressure in int. j g^{-1} °K^{-1} is

$$S^\circ_{1\ atm} - S_{sat.} = R\left(\frac{k}{V_{sat.}T^2} + \ln\frac{R'T}{p_{1\ atm}V_{sat.}}\right),$$

where the constants and the properties of the gas are expressed in the same units as those given above for the enthalpy difference, except for the gas constant R', which is in units consistent with those used for p, V, and T. With p expressed in atmospheres and $V_{sat.}$ in ml g^{-1}, R' is 1.4625 atm ml g^{-1} °K^{-1}.

Table 6 gives values of the enthalpy of *cis*-2-butene at intervals of 5 degrees between 245° and 300°K and at 298.16°K (25°C) derived from calorimetric and vapor-pressure data. In column 2 are values of the enthalpy of the saturated liquid from table 1. In column 3 are values of the enthalpy of vaporization calculated by means of equation 4. The values at 295°, 298.16°, and 300°K are extrapolations above the range of temperatures included in the measurements of heats of vaporization, but it is improbable that a significant error resulted from the extrapolation. Column 4 gives values of the enthalpy of the saturated vapor, column 5 the differences between the enthalpy of the ideal gas and that of the saturated vapor, and column 6 the enthalpy of the ideal gas. In column 7 are values of the specific heat at constant pressure, C_p°, of the ideal gas. Column 7 entries are actually values of $\Delta H^\circ/\Delta T$ with ΔT=10 degrees. Since dH°/dT is not changing rapidly, the ratio of these finite differences is very nearly equal to the derivative.

Table 7 is similar to table 6, except that corresponding values of entropy are given.

TABLE 6.—*Enthalpies, heat of vaporization, and specific heat of cis-2-butene derived from calorimetric and vapor-pressure data*

[The superscript (°) designates the ideal gas state. E_0^* is the internal energy of solid *cis*-butene at 0°K. 13.4114 cal $mole^{-1}$=1 int. j g^{-1}. Atomic weights: C=12.010, H=1.008]

T	$(H_{sat.\ liq.}-E_0^*)$	L_s	$(H_{sat.\ vap.}-E_0^*)$	$H^\circ-H_{sat.\ vap.}$	$(H^\circ-E_0^*)$	$C_p^\circ=\frac{dH^\circ}{dT}$
°K	*Int. j* g^{-1}	*Int. j* g^{-1}	*Int. j* g^{-1}	*Int j* g^{-1}	*Int. j* g^{-1}	*Int. j* g^{-1} °K^{-1}
245	453.09	445.58	898.67	1.36	900.03	----------
250	463.44	441.21	904.65	1.68	906.33	1.262
255	473.85	436.75	910.60	2.05	912.65	1.267
260	484.34	432.19	916.53	2.47	919.00	1.277
265	494.91	427.54	922.45	2.97	925.42	1.288
270	505.56	422.79	928.35	3.53	931.88	1.299
275	516.30	417.95	934.25	4.16	938.41	1.316
280	527.15	413.01	940.16	4.88	945.04	1.332
285	538.08	407.97	946.05	5.68	951.73	1.352
290	549.13	402.85	951.98	6.58	958.56	1.375
295	560.28	397.62	957.90	7.58	965.48	1.398
298.16	*567.41*	*394.27*	*961.68*	*8.27*	*969.95*	----------
300	571.56	392.30	963.86	8.68	972.54	1.423

TABLE 7.—*Entropies of cis-2-butene derived from calorimetric and vapor-pressure data*

[The superscript (°) designates the standard ideal gas state. Entropy, S, of the solid at 0°K equals zero. 13.4114 cal mole^{-1}=1 int. j g^{-1}. Atomic weights: C=12.010, H=1.008]

T	$S_{sat.\ liq.}$	$\Delta S=L_v/T$	$S_{sat.\ vap.}$	$S^\circ_{1\ atm.}-S_{sat.\ vap.}$	$S^\circ_{1\ atm.}$
°K	*Int. j g^{-1} °K^{-1}*	*Int. j g^{-1} °K^{-1}*	*Int. j g^{-1} °K^{-1}*	*Int. j g^{-1} °K^{-1}*	*Int. j g^{-1} °K^{-1}*
245	3.4985	1.8187	5.3172	−0.2037	5.1135
250	3.5403	1.7648	5.3051	−.1664	5.1387
255	3.5814	1.7127	5.2941	−.1305	5.1636
260	3.6221	1.6623	5.2844	−.0960	5.1884
265	3.6623	1.6134	5.2757	−.0627	5.2130
270	3.7020	1.5659	5.2679	−.0311	5.2368
275	3.7414	1.5198	5.2612	−.0005	5.2607
280	3.7803	1.4750	5.2553	+.0292	5.2845
285	3.8190	1.4315	5.2505	+.0579	5.3084
290	3.8572	1.3891	5.2463	+.0857	5.3320
295	3.8952	1.3479	5.2431	+.1127	5.3558
298.16	*3.9191*	*1.3223*	*5.2414*	*+0.1294*	*5.3708*
300	3.9330	1.3077	5.2407	+0.1389	5.3796

IX. ESTIMATES OF PROBABLE ERRORS IN THE MEASUREMENTS AND IN THE VALUES OF PROPERTIES DERIVED FROM THE CALORIMETRIC DATA

The accuracy of measurements made with the calorimeter used for the *cis*-butene investigation is discussed in more detail, with a description of the calorimeter, in a paper on an investigation of butadiene [2].

The probable error[4] assigned to specific-heat values in table 1 above 40°K is 0.1 percent and to the heat of fusion, 0.07 percent. It is believed that, as a result of increased experience, the probable error of measurement of heats of vaporization of *cis*-butene is 0.1 percent instead of the 0.15 percent for the butadiene investigated earlier. Errors in the temperature scale are on the average much smaller than 0.1 percent of the absolute temperature, hence they do not introduce appreciable calorimetric errors. The enthalpy and entropy of solid *cis*-butene at 40°K are small compared with the enthalpy and entropy of the liquid, hence even though the errors in specific-heat determinations are probably larger than 0.1 percent below 40°K, these errors below 40°K have little effect upon the errors in the enthalpy and entropy values given in tables 1, 6, and 7 for the liquid.

The effect of impurities on the specific heat is another possible source of error that should be considered, although it cannot be evaluated in the present experiment. In measurements on butadiene [2], the specific heat of the solid seemed to be rather sensitive to a small impurity, although the specific heat of the liquid was unaffected. The specific heat at 80°K of a sample of solid butadiene that contained 0.055 mole percent of impurity was more than 1 percent higher than that of a pure sample. This difference between the pure and slightly impure samples diminished rapidly at higher and lower temperatures, but it was appreciable over a temperature range of 50 degrees. Since the present measurements were made on only one sample of *cis*-2-butene, no information concerning the effect of impurities was obtained.

[4] As used in this paper, the term "probable error" is the author's estimate of that error which is just as likely to be exceeded as not. Actual computations of probable error were not carried out, because in some cases systematic errors may have been much larger than accidental errors, and in other cases there were insufficient data to justify such a computation.

Leaving out any errors that might have resulted from impurities, it is reasonable to assign a probable error of 0.1 percent to the values of the entropy and enthalpy of the saturated vapor in tables 6 and 7.

In estimating the errors in the values of the enthalpy and entropy of the ideal gas in tables 6 and 7, it is necessary to consider the error in the equation of state used to determine the differences between the properties of the real and ideal gas. In figure 2, it appears that a probable error of 10 percent should be assigned to the selected value (1.075×10^6 ml g^{-1} $°K^2$) of k. This corresponds to an error in $(H°-E_0^s)$ of 0.015 percent at 245°K and about 0.09 percent at 300°K. By combining the probable error of the calorimetric measurements with the probable error arising from the equation of state, the probable error of the values of $(H°-E_0^s)$ in table 6 is 0.11 percent at 245°K and increases to 0.14 percent at 300°K. An error of 10 percent in the value of k will cause an error of only 0.03 percent in the value of $S°$ at 300°K, hence the probable error to be assigned to the values of $S°$ in table 7 is 0.13 percent.

Since an average slope of an $(H°-E_0^s)$ versus T graph may be determined from values of $(H°-E_0^s)$ at the two ends of the graph, the probable error of the slope $dH°/dT=C_p^o$ was estimated from values of the probable errors in $(H°-E_0^s)$ at 245° and 300° K. The probable error obtained for C_p^o values in table 6 is about 0.030 j g^{-1} $°K^{-1}$, or 2.3 percent.

X. COMPARISON OF RESULTS OF THE CALORIMETRIC AND VAPOR-PRESSURE MEASUREMENTS WITH RESULTS OF OTHER OBSERVERS

Todd and Parks [6] measured the specific heat of *cis*-2-butene from 90° to 266° K. The values they report are, in general, somewhat larger than the values given in this paper. The discrepancy is greatest at temperatures between 110° and 170° K, attaining a maximum value of 0.9 percent. At both ends of the temperature range they covered the agreement is good, about 0.2 percent. The heat of fusion reported by Todd and Parks is only 0.1 percent higher than that obtained in this investigation.

The vapor pressure of *cis*-2-butene has been reported by Lamb and Roper [7], and by Kistiakowsky, Ruhoff, Smith, and Vaughan [8]. Figure 3 shows the deviations of the reported values from equation 5. The values reported by these observers are somewhat higher than those obtained in this investigation. Since two of the impurities, *trans*-2-butene and air, likely to be present in *cis*-2-butene have higher vapor pressures than *cis*-butene, it is believed that the lower values obtained in this investigation are an indication of a purer sample.

The specific heat of gaseous *cis*-2-butene was determined by Kistiakowsky and Rice [9], who used an adiabatic expansion method by which the heat capacity is determined from the change in temperature that results from an isentropic expansion. The equation of state of the gas is important for this method, since, in effect, the specific heat is determined from the ratio of the work done by the gas in the isentropic expansion to the measured change of temperature, and the work done is calculated with the aid of the equation of state of the gas. Table 8 shows the dependence upon the equation of state of the specific heats of *cis*-2-butene determined by the adiabatic expansion method. The authors of the present paper prefer

equation of state 9 to the equation of state proposed by Roper [5]. The 10-percent probable error that the authors have placed upon the constant k in equation of state 9 gives rise to the following probable errors in the specific heats: (1) in C_p at 1 atm, at 298.58° K, 0.0077 int. j g^{-1} °K^{-1}; at 332.85°, 0.0063; and at 371.24°, 0.0050 int. j g^{-1} °K^{-1}; (2) in C_p° at 298.58° K, 0.0052 int. j g^{-1} ° K^{-1}; at 332.85°, 0.0044; and at 371.24°, 0.0036.

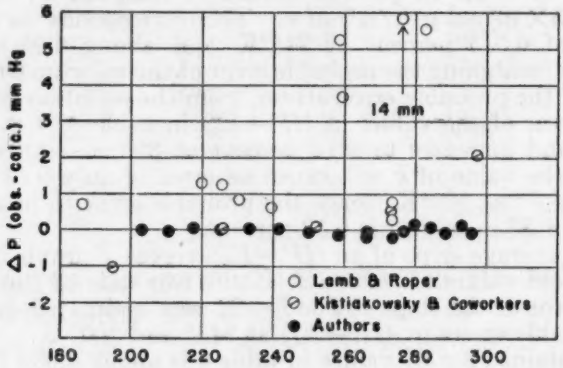

FIGURE 3.—*Deviations of observed vapor pressures from equation 5.*

TABLE 8.—*Heat capacities of gaseous cis-2-butene: (1) as reported by Kistiakowsky and Rice [9], who used Roper's equation of state, (2) as calculated from the data of Kistiakowsky and Rice by using the equation of state, eq 9, of this paper, and (3) as calculated from spectroscopic data*

[The superscript (°) refers to the ideal gas state. 13.4114 cal $mole^{-1}$=1 int. j g^{-1}. Atomic weights: C=12.010, H=1.008]

T	From the paper of Kistiakowsky and Rice, using the conversion factor in their paper 9 and —			From experimentat data of Kistiakowsky and Rice and equation of state [9] of the present paper		Calculated from spectroscopic data
	Equation of state, $pV=RT$	Roper's equation of state				
	C_p'	Real gas C_p at 1 atm	C_p°	Real gas C_p at 1 atm	C_p°	C_p°
° K	*Int. j* g^{-1} ° K^{-1}	*Int. j* g^{-1} ° K^{-1}	*Int. j* g^{-1} ° K^{-1}	*Int. j* g^{-1} ° K^{-1}	*Int. j* g^{-1} ° K^{-1}	*Int. j* g^{-1} ° K^{-1}
298.58	1.377	1.496	1.446	1.454	1.429	1.432
332.85	1.519	1.606	1.572	1.582	1.563	1.565
371.24	1.675	1.737	1.716	1.725	1.711	1.718

The experimental value of C_p° for gaseous *cis*-2-butene derived from the vapor-pressure and calorimetric measurements on the liquid reported in this paper (see table 6) is 1.416 int. j g^{-1} ° K^{-1} at 298.58° K. This is 2.1 percent lower than the value of Kistiakowsky and Rice based on Roper's [5] equation of state, and 0.9 percent lower than the value derived from the experimental data of Kistiakowsky and Rice, using the equation of state 9. In section IX it is shown that the probable error in the values of C_p° derived from the experimental data reported in this paper, based upon probable errors from all sources, was 2.3 percent. The agreement of the C_p° values derived from our

measurements with the values in table 8 derived from direct measurements on the gas by Kistiakowsky and Rice is a confirmation of the accuracy of the present measurements in the range 245° to 300° K.

XI. THERMODYNAMIC FUNCTIONS FROM 300° TO 1,500° K DERIVED FROM SPECTROSCOPIC DATA

Gershinowitz and Wilson [10] investigated the infrared absorption and Raman spectra of *cis-* and *trans*-2-butene. Their measurements covered the full range of the fundamental frequencies of the intramolecular motions. Weak lines were measured, and in the case of *trans*-2-butene the polarization of the Raman lines was determined. Polarization data on *cis*-2-butene were not reported.

Because the *cis*-2-butene molecule has C_{2v} symmetry, all internal motions are optically active, and all are allowed in both the infrared and Raman spectra with the exception of the A_2 vibrations (symmetrical with respect to C_{2v} axis and asymmetrical with respect to the σ_x and σ_y planes), which are forbidden in the infrared absorption spectra.

In working out an assignment of frequencies, use was made of the *trans*-2-butene assignment which had previously been worked out [11]. Because of the C_{2h} symmetry of *trans*-2-butene, the fundamental vibrations are either Raman or infrared active, but not both. This with the Raman polarization observations of *trans*-2-butene make possible a more certain assignment of frequencies. In the assignment of the carbon skeleton frequencies, the *cis-trans* relationships in the spectra of 1,2-dichloroethylene and 1,2-dibromoethylene [12] served as a guide in the use of the *trans*-2-butene frequencies. The results of O. Burkard's normal coordinate calculation [12] were helpful also.

The frequencies in reciprocal centimeters used for the calculation of the thermodynamic properties of *cis*-2-butene from 300° to 1,500° K were as follows:

C *skeleton frequencies*—

A_1: ω_1, 1669; ω_2, 883; ω_3, 304.
A_2: ω_6, 402.
B_2; ω_4, 986; ω_5, 583.

Frequencies due to C–H *groups*—

δ's: 1233, 1267.
γ's: 1018, 1047.

Frequencies due to CH_3 *groups*—

δ's: 1267, 1389, 1436, 1462, 1473, 1541,.
γ's: 685, 883, 1047, 1233.

C–H *stretching frequencies*—

ν's: 2874, 2877, 2931(2), 2979(2), 3034(2).

The C=C torsional frequency, ω_6 for *cis*-2-butene was estimated by Harold W. Woolley, who used a force-constant calculation based on the frequencies of other molecules. If we consider the two halves of the molecule as rigid, the estimate based on the C=C torsion in ethylene was 535 cm^{-1}. The estimate based on the value 270 cm^{-1}

assumed [11] for the C=C torsional frequency, ω_6 in *trans*-2-butene was 470 cm^{-1}. The sign of the difference [ω_6 (*cis*)$-\omega_6$ (*trans*)] was easily verified from general considerations for the case of identical torsional constants. A more detailed calculation was made in which bonds attached to the doubly bonded carbons were assumed to be equally flexible for all directions of bending, with bending constants determined from other molecules. As before, the ethylene torsional frequency was used to evaluate a torsion constant for the double bond. Torsional frequencies thus estimated were 374 cm^{-1} for *cis*-dichloroethylene, 342 cm $^{-1}$ for *cis*-dibromoethylene, and 368 cm^{-1} for *cis*-2-butene. These estimated frequencies for *cis*-dichloroethylene and *cis*-dibromoethylene are 31 cm^{-1} and 30 cm^{-1}, respectively, lower than the observed frequencies assigned by Kohlrausch [12] to these ethylene halides. The assignment of the observed *cis*-2-butene frequency 402 cm^{-1} to the torsional vibration, ω_6 appeared logical, since the difference 34 cm^{-1} between the assigned and estimated values for *cis*-2-butene is nearly the same as the differences for the ethylene halides.

The following bond lengths and angles were assumed for *cis*-2-butene: C=C distance, 1.36 A; C−C distance, 1.54 A; C−H distance, 1.09 A; $\angle$H−C−H =109°28′; $\angle$C−C=C=125°16′; $\angle$H−C−C =109°28′. From these assumed values it follows that the product of the principal moments of inertia, *ABC*, is 1.85×10^{-114} g^3 cm^6 and the reduced moment of inertia for each rotating methyl group is 5.02×10^{-40} g cm^2 [12].

Good agreement of spectroscopic values for the specific heat of gaseous *cis*-2-butene with the calorimetric values is obtained with a value of 700 cal $mole^{-1}$ for the barriers restricting internal rotation of the methyl groups. Table 8 shows the agreement. Agreement of the absolute values and the trends with temperature are significant. The calorimetric value for the entropy, $S°$, of *cis*-2-butene in the ideal gas state at 300° K is 72.148 cal $mole^{-1}$ $°K^{-1}$. A probable error of ±0.094 cal $mole^{-1}$ $°K^{-1}$ was assigned to the calorimetric value at 300° K. The difference between the spectroscopic and calorimetric values is 0.210 cal $mole^{-1}$ $°K^{-1}$. The authors consider this agreement of the spectroscopic and calorimetric entropy values satisfactory after making allowances for (1) the uncertainties in the experimental values of the specific heat C_p°, (table 8) from which the barrier of 700 cal $mole^{-1}$ was calculated, and in the assumption that the barriers to rotation of the two methyl groups can be represented by two independent barriers of the form $V=(1/2)\ V_0\ (1-\cos 3\theta)$, and (2) for a possible effect of impurities in the *cis*-butene sample on the calorimetric value for $S°$ (see section IX).

In tables 9 and 10 are tabulated the thermodynamic functions for *cis*-2-butene in the ideal gas state calculated with barriers of 700 cal $mole^{-1}$ restricting rotation of the methyl groups and with the preceding frequency assignment. The contributions to the thermodynamic functions arising from hindered rotation were calculated with the aid of the 1942 tables published by Pitzer and Gwinn [13]. The principles and methods involved in the calculations have been discussed by Aston [14].

TABLE 9.—*Thermodynamic functions of cis-2-butene in the idea gas state*

[$H°$ and $E°_0$ are enthalpies at $T°$ and 0°K, respectively, referred to the enthalpy of the elements in the standard state at 0°K. $\Delta H°$ is the heat of formation from the elements in their standard states at $T°$K. $H°_0 - E°_0 = 3{,}670$ cal mole^{-1}. 13.4114 cal mole^{-1} = 1 int. j g^{-1}. Atomic weights: C = 12.010, H = 1.008]

T	$\frac{H°-E°_0}{T}$	$H°$	$\Delta H°$	$C°_p$
°K	cal °C^{-1} mole^{-1}	cal mole^{-1}	cal mole^{-1}	cal °C^{-1} mole^{-1}
298.16	13.50	7,700	−1,400	19.17
300	13.53	7,730	−1,440	19.27
400	15.63	9,920	−3,020	24.56
500	17.93	12,630	−4,370	29.57
600	20.24	15,810	−5,490	33.96
700	22.48	19,410	−6,380	37.74
800	24.60	23,350	−7,090	41.00
900	26.59	27,600	−7,620	43.83
1,000	28.44	32,110	−8,010	46.28
1,100	30.16	36,840	−8,280	48.41
1,200	31.76	41,780	−8,430	50.25
1,300	33.24	46,890	−8,490	51.85
1,400	34.62	52,140	−8,490	53.23
1,500	35.90	57,520	−8,440	54.44

TABLE 10.—*Thermodynamic functions of cis-2-butene in the ideal gas state at 1-atmosphere pressure*

[$F°$ and $E°_0$ are the free energy at $T°$K and the internal energy at 0°K, respectively, referred to the internal energy of the elements in their standard states at 0°K. $\Delta F°$ and K are the free-energy changes and equilibrium constants, respectively, for the reaction forming *cis*-C_4H_8 from its elements at $T°$K. $E°_0 = 3{,}670$ cal mole^{-1}. 13.4114 cal mole^{-1} = 1 int. j g^{-1}. Atomic weights: C = 12.010, H = 1.008]

T	$-\left(\frac{F°-E°_0}{T}\right)$	$S°$	$-F°$	$\Delta F°$	$\log_{10} K$
°K	cal °C^{-1} mole^{-1}	cal °C^{-1} mole^{-1}	cal mole^{-1}	cal mole^{-1}	$\frac{-\Delta F°/RT}{2.3026}$
298.16	58.32	71.82	13,720	16,030	−11.763
300	58.41	71.94	13,850	16,140	−11.757
400	62.59	78.22	21,370	22,230	−12.151
500	66.32	84.24	29,490	28,710	−12.553
600	69.79	90.03	38,200	35,440	−12.910
700	73.07	95.56	47,480	42,340	−13.221
800	76.21	100.81	57,300	49,360	−13.485
900	79.22	105.81	67,630	56,440	−13.708
1,000	82.12	110.56	78,450	63,590	−13.898
1,100	84.91	115.07	89,730	70,760	−14.059
1,200	87.61	119.37	101,460	77,950	−14.197
1,300	90.21	123.46	113,600	85,140	−14.314
1,400	92.73	127.35	126,150	92,340	−14.415
1,500	95.16	131.06	139,080	99,540	−14.504

The internal energy, or enthalpy, of *cis*-2-butene in the ideal gas state at 0°K, that is $E°_0$, was calculated by using (1) the value −29,820 cal mole^{-1} of Prosen and Rossini [15] for $\Delta H_{298.16°}$, the enthalpy change for the formation of gaseous *n*-butane from its elements in their standard states at 25°C; (2) the value of Kistiakowsky, Ruhoff, Smith, and Vaughan [8], −28,570 cal mole^{-1}, for $\Delta H_{355°}$, the enthalpy change for the gas-phase hydrogenation of *cis*-2-butene to *n*-butane at 355°K corrected to the new atomic weight of carbon; (3) 1,408 cal mole^{-1} for the difference between the enthalpies of gaseous *n*-butane at 355° and 298.16°K [11]; (4) enthalpy differences for *cis*-2-butene

from table 9; and (5) enthalpies of C and H_2 from reference [16]. The value obtained for E_0° was 3,670 cal mole^{-1}.

The value of E_0° for *trans*-2-butene is 2,455 cal mole^{-1} [11], and accordingly the heat of the *cis-trans* isomerization of 2-butene at 0°K is 1.2 kcal mole^{-1}. The greater energy of *cis*-butene is attributed principally to mutual potential energy of the methyl groups, which, in *cis*-butene, are in close proximity.

The low value, 700 cal mole^{-1}, for the barriers restricting rotation of the methyl groups in *cis*-butene is interesting in view of this closeness of approach of the methyl groups and the possible steric hindrance when in rotation. In *trans*-butene, in which the groups are well separated, the barriers are 1,900 cal mole^{-1} [11]. Although the difference between the maximum and minimum values of the potential energy of the field in which the methyl groups rotate is smaller for *cis*-butene than for *trans*-butene, the minimum value of the potential is higher for *cis*- than *trans*-butene. This is inferred from the higher value of E_0° for *cis*-butene than for *trans*-butene. Consideration of repulsions between hydrogen atoms in a Fischer-Hirschfelder model for *cis*-butene makes it seem plausible that the difference between the maximum and minimum values of the potential restricting rotation of the methyl groups should be small. With the model, one sees that as the methyl groups rotate hydrogen atoms are so close for all orientations of the methyl groups that there is no place where the minimum in potential can be very low.

Pitzer and Scott [18] obtained 2,000 cal mole^{-1} for the barriers restricting rotation of the methyl groups in *ortho*-xylene. In *ortho*-xylene and in *cis*-2-butene the relative spatial positions of the two methyl groups and the two proximate nonmethyl hydrogen atoms are similar. However, in *cis*-butene the separation of the two methyl groups is somewhat greater than in *ortho*-xylene, and the separation of the nonmethyl hydrogen and methyl group somewhat less. If repulsions between H atoms are a determining factor for barriers, a lower barrier in *cis*-2-butene is reasonable.

XII. *CIS-TRANS* ISOMERIZATION OF 2-BUTENE

In table 11 are given for the *cis-trans* isomerization of 2-butene

$$\textit{cis}\text{-2-butene} \rightleftharpoons \textit{trans}\text{-2-butene}$$

in the ideal gas state, the following properties: (1) the heat of isomerization, equal to $-\Delta H^\circ$; (2) the standard entropy change; (3) the standard free-energy change; (4) the equilibrium constant, K, equal to $\exp.(-\Delta F^\circ/RT)$; and (5) the equilibrium proportion of *trans*-2-butene in a mixture of *cis-trans* isomers, equal to $K/(1+K)$. The *cis*-2-butene data used in compiling table 11 were taken from tables 9 and 10, and the *trans*-2-butene data from reference [11]

TABLE 11.—*Standard enthalpy, entropy, and free-energy changes, equilibrium constant, and equilibrium concentration for the reaction cis-2-butene ⇌ trans-2-butene in the ideal gas state*

T	Heat of reaction, $-\Delta H^\circ$	Standard entropy change, ΔS°	Standard free-energy change, ΔF°	Equilibrium constant, K $\frac{[trans\text{-}C_4H_8]}{[cis\text{-}C_4H_8]}$	Equilibrium proportion, $\frac{[trans\text{-}C_4H_8]}{[cis+trans\ C_4H_8]}$
°K	*cal mole*$^{-1}$	*cal mole*$^{-1}$	*cal mode*$^{-1}$		
298.16	1,045	−3.50	−778	3.72	0.788
300	1,048	−3.49	−779	3.70	.787
400	899	−2.25	−749	2.57	.720
500	790	−1.580	−684	1.99	.666
600	752	−1.253	−675	1.76	.638
700	688	−0.983	−701	1.66	.624
800	594	−.743	−719	1.57	.611
900	517	−.574	−759	1.53	.605
1,000	487	−.487	−789	1.49	.598
1,100	507	−.461	−885	1.50	.600
1,200	527	−.439	−927	1.48	.597
1,300	541	−.416	−973	1.46	.593
1,400	469	−.335	−972	1.42	.587
1,500	276	−.184	−1,004	1.40	.583

TABLE 12.—*Comparison of equilibrium constants K for the reaction cis-2-butene ⇌ trans-2-butene*

[Derived from (1) calculations based on spectroscopic data, (2) catalyzed equilibrium concentrations of C_4 hydrocarbons measured by Frey and Huppke [19], and (3) short-period uncatalyzed thermal-decomposition products of *n*-butene and *iso*pentane by Frey and Hepp [20]]

T	K (spectroscopic values from table 11)	K (experimental values)*	Source of experimental value
°K			
623	1.74	1.7 and 1.6, (1.6)	Frey and Huppke [19].
673	1.68	1.5, (1.6)	Do.
723	1.64	1.4, (1.6)	Do.
848	1.55	2.1 and 1.7	Frey and Hepp [20].

* The values in parentheses were obtained from Frey and Huppke's equilibrium constants for the dehydrogenation reactions of *n*-butane to *trans*-2-butene and to *cis*-2-butene. $K(cis \rightarrow trans\text{-butene}) = K(n\text{-butane} \rightarrow trans\text{-butene})/K(n\text{-butane} \rightarrow cis\text{-butene})$. Values not in parentheses are ratios of the measured *trans-cis* butene concentrations. The 2 sets of Frey and Huppke values in column 3 are based on the same *cis*- and *trans*-2-butene concentration data and should agree within experimental accuracy.

As with other isomerization reactions, the equilibrium constant, K, and the equilibrium proportions of the *cis* and *trans* isomers are independent of pressure.

Frey and Huppke [19] measured the concentrations of the isomeric butenes in equilibrium with normal butane at 350°, 400°, and 450° C. In their investigation, equilibrium was established by passing the vapors over a heated chromium-oxide catalyst. The Frey and Huppke experimental values for K without parentheses in column 3 of table 12 are ratios of their measured equilibrium concentrations of the *trans* and *cis* isomers. The values in parentheses are ratios of Frey and Huppke's equilibrium constants for the dehydrogenation reactions of *n*-butane to *trans*- and to *cis*-2-butene: $K(cis \rightarrow trans\text{-2-butene}) = K(n\text{-butane} \rightarrow trans\text{-2-butene})/K(n\text{-butane} \rightarrow cis\text{-2-butene})$. The two sets of Frey and Huppke values in column 3 are based on the same *cis*- and *trans*-2-butene concentration data and should agree witnin experimental error. Frey and Hepp [20] measured the concentrations of the *cis* and *trans* isomers of 2-butene in the primary products of the

uncatalyzed thermal decomposition of *n*-butane and *iso*pentane at 575° C for 25 seconds and 12 seconds, respectively.

The spectroscopic and experimental values of K agree within the limits of error of the experimental data.

The authors are indebted to M. R. Fenske for the preparation of a pure sample of *cis*-2-butene for these measurements. The authors are also indebted to Harold W. Woolley and Morris Moskow for help with the calculations of properties from spectroscopic data.

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A DAILY RECORD OF ULTRAVIOLET SOLAR AND SKY RADIATION IN WASHINGTON, 1941 TO 1943

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ABSTRACT

A description is given of a photoelectric ultraviolet-intensity meter and automatic integrating and recording apparatus for measuring the biologically effective component of ultraviolet radiation, of wavelengths 3132 A and shorter, from the sun and the entire sky, incident on a horizontal plane, under various meteorological conditions. Methods of standardization, in absolute value, are described (see RP1542 for supplementary data). A continuous graphical record of the integrated daily total amount of biologically effective ultraviolet solar and sky radiation observed during a period of 3 years (1941 to 1943) in Washington, D. C. is given. The monthly totals of biologically effective ultraviolet, in absolute value (milliwatt minutes per square centimeter) mw min/cm² are also given graphically. On the clearest days the biologically effective component of ultraviolet radiation of wavelengths 3132 A and shorter, incident from the sun and the whole sky at midday, ranges from about 180 microwatts per square centimeter, (μw/cm²) in midsummer to about 30 μw/cm² in midwinter. A series of erythema tests is given, correlating the physical (radiometric) measurements with the physiological reaction of the untanned skin, which information is of interest in helotherapy and bioclimatology.

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I. INTRODUCTION

An important problem in bioclimatology is the securing of a continuous radiometric record of the total daily amount of biologically effective ultraviolet radiation from the sun and from the entire sky, incident on a horizontal plane, as a function of the season and the geographic latitude [1, 6].[1]

As noted in a previous paper [2], the evaluation of the biologically effective ultraviolet solar radiation is still in its infancy, and the uncertainties involved are somewhat comparable with those experienced in the beginning of the evaluation of the total incident solar radiation of all wavelengths half a century ago. However, there is

[1] Numbers in brackets indicate the literature references and notes at the end of this paper.

this distinction, that whereas the evaluation of the total solar radiation is made with a radiometer that is practically nonselective to all the wavelengths incident on the earth's surface and can be easily calibrated in absolute units, the evaluation of the biologically effective ultraviolet component of sky and solar radiation is made with a radiometer that is selectively responsive to only a narrow band of wavelengths, and hence is difficult to calibrate in absolute units.

A further difficulty arises from the fact that the energy value of the biologically effective component of ultraviolet radiation of wavelengths 3132 A and shorter usually is less than a thousandth part of the total incident solar radiation. Hence, a much more sensitive (consequently less stable) radiometer is required to evaluate the ultraviolet component than the total incident solar and sky radiation of all wavelengths.

Variations in ozone concentration in the stratosphere and atmospheric pollution by smoke and dust have a greater effect upon the ultraviolet radiation of short wavelengths than upon the longer wavelengths included in the measurement of the total incident solar and sky radiation. Hence, the total amount of ultraviolet radiation received at two closely situated stations (especially in thickly populated localities) may differ greatly, depending upon dust, smoke, and the direction of the prevailing wind. It is therefore, a question of the extent of the refinements in accuracy that should be attempted in a long-range daily evaluation of biologically effective ultraviolet solar and sky radiation of interest in climatology, as differing from a highly accurate evaluation in connection with an irradiation test of short duration, involving a specific biological (erythemal, antirachitic, tanning, etc.) reaction.

In the present investigation the type of construction of a standard ultraviolet solar and sky intensity meter that will operate continuously under extreme weather conditions (heat, cold, snow, rain, sunshine) could not be anticipated without preliminary experiments. Earlier efforts were begun about 9 years ago when the problem was presented to secure a continuous record of the total incident, biologically effective ultraviolet solar and sky radiation [3, 18, 19, 20] for use in irradiating animals.

The data summarized in the present paper were obtained as a by-product in connection with an investigation of photoelectric instruments and methods of measuring ultraviolet solar and sky radiation incident on a horizontal plane, useful in heliotherapy [1, 3]. This investigation has involved an examination of the response (with respect to wavelength and angle of incidence of the exciting radiation), and the constancy of performance under normal operation, of more than a dozen phototubes [7] of Mg [3] and of Ti and Zr [8], some of which were constructed for study by one of the writers [1]. Others were constructed for field use by the Department of Agriculture [24] and by the National Institute of Health [8] and for use as primary standards to be maintained by the National Bureau of Standards [4].

As was to be expected, with the development and improvement in performance of suitable photoelectric cells, this type of ultraviolet intensity meter is finding applications in other fields, for example, in connection with tests of weathering of materials (cotton) in the field [24].

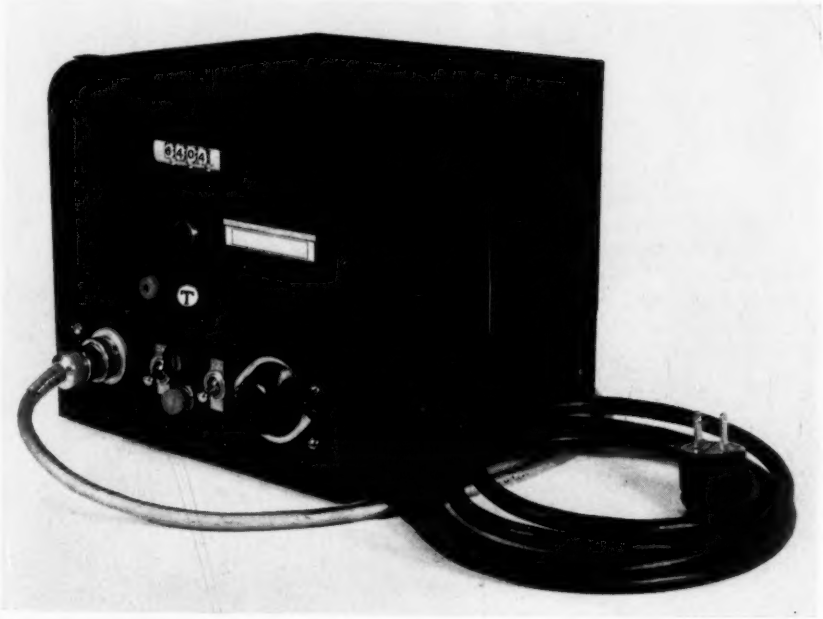

FIGURE 1.—*Metal box containing rectifier tubes, relay, and an impulse ("message") counter.*

Connection with automatic impulse counter and recorder is made at *T*. The right-hand outlet is not visible.

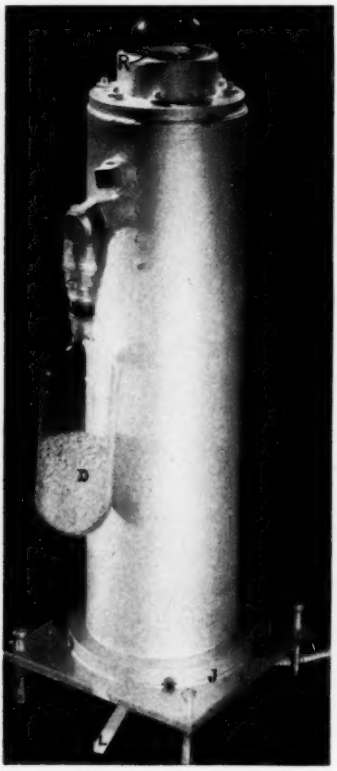

FIGURE 2.—*Mg-phototube in brass housing containing two "trigger tubes," air condenser, and drying material, D.*

Lever arm, *L*, is for interchanging trigger tubes. The photosensitive receiver, *R*, measures the ultraviolet solar and sky radiation incident on a horizontal plane. The bright spots are unavoidable reflections of the light sources used in making the photograph—see figure 3.

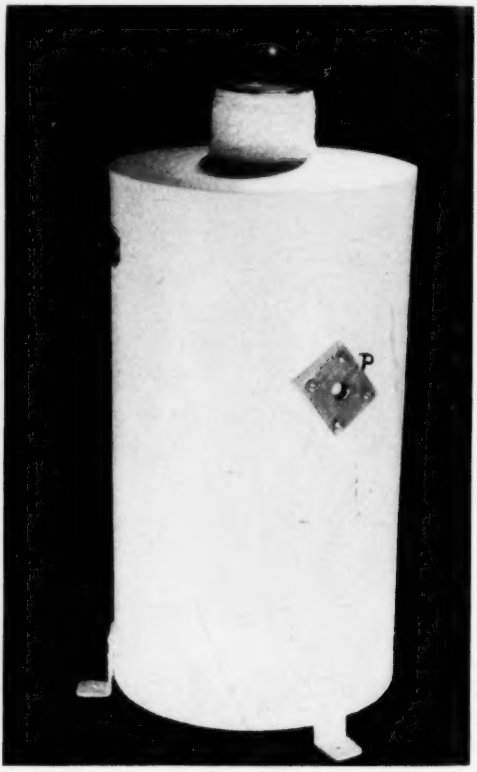

FIGURE 3.—*Zr-phototube supported in metal housing.*

Shadowing device is attached at *P*.

As already noted, the securing of statistical data on ultraviolet solar and sky radiation of use in bioclimatology is just beginning. In this connection, reference is made to two researches. The first is by Kenrick and his collaborators [19, 20, 21], who measured ultraviolet intensities from the sun and from an appreciable portion of the surrounding sky in San Juan, P. R., using a Ti-phototube mounted upon a polar axis, whereby the semicylindric receiver was kept directed normal to the incident solar radiation [3, 18]. The measurements were continued for 2 years (1937–39). The sensitivity of the phototube was checked periodically by means of a quartz mercury-arc lamp calibrated against the Bureau's primary standard of ultraviolet radiation [11]. Outstanding among their observations is an increase in ultraviolet radiation by reflection from clouds—a phenomenon that will be discussed in the present paper.

The second paper of interest in bioclimatology, by Luckiesh and his collaborators [22], gives a continuous 4-year record (1935–38, inclusive) of ultraviolet solar and sky radiation incident on a horizontal plane in the suburbs of Cleveland, Ohio. The photoelectric cell was a pear-shaped glass bulb, about 6 cm in diameter, the interior of which was sensitized by an opaque layer of cadmium, with a clear area about 3 cm in diameter on one side of the glass bulb to admit solar and sky radiation to the photosensitive interior (see fig. 1 of RP1075 [17a]. Outstanding among their observations is the large amount of ultraviolet radiation received from the whole sky, as herein recorded and as previously noted, particularly by Dannmeyer [4, 23]. Based upon observations of this type, heliotherapy by sky irradiation may prove useful in cases where direct solar irradiation cannot be employed [35].

II. INSTRUMENTS AND METHODS

Taking into consideration ever-changing sky conditions, it is desirable to use a quick-acting, integrating ultraviolet radiant-flux meter to secure climatological data on the amount of biologically effective ultraviolet solar and sky radiation incident at a given station.

The particular ultraviolet radiant-flux integrating device investigated consisted of three parts: (a) an electronic integrating device, comprising a new type of phototube for intercepting ultraviolet solar and sky radiation incident on a horizontal plane [3], an electric condenser, and a grid-glow ("trigger") tube [5], which combination was inclosed in a suitable chamber that was mounted on the roof of a building, (b) a metal box (fig. 1), within the laboratory, containing a relay, rectifier tubes, and an impulse ("message") counter [5] made by R. J. Cashman [3]; and, supplementing this counter, (c) an automatic impulse counter and recorder, consisting of a modified commercial photoelectrically operated traffic recorder that was connected (at *T* in fig. 1) in parallel with the impulse counter. This recorder registered the impulses received from the photoelectric integrator, and, at quarter-hour intervals, printed on a strip of paper [4] the day, the hour, and quarter-hour, and the total number of incoming impulses. In this manner, in addition to the reading on the impulse (message) counter, a permanent printed record was obtained of the number of impulses and, hence of the total amount of ultraviolet solar and sky radiation. Controlled by an a-c-driven clock, the ultraviolet inte-

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grating meter and recorder were operated only during the daytime.

It is relevant to note that in the operation of the device, the photoelectric cell, on exposure to ultraviolet radiation, emits electrons, i. e., conducts a current that charges a condenser to a critical voltage, at which voltage the condenser is discharged through an impulse-counting mechanism, and that the charging of the condenser is repeated at a rate that is proportional to the intensity of the incident ultraviolet radiation, which varies with the solar altitude and with ever-changing weather conditions. Knowing the energy required to charge the condenser to a critical voltage (the "microwatt-seconds" factor, I, for converting an impulse into energy units), it is a simple matter to obtain from the printed record the number of impulses per unit time (half-hour, hour, day), and hence the total amount of biologically effective ultraviolet radiation received each day.

In some of the Eppley thermoelectric pyrheliometers (Kimball design [25]) for measuring solar and sky radiation incident on a horizontal plane the voltage conversion-factor (millivolts per gram-calory) is the same for all solar heights. Similarly, the finding of a photoelectric cell having the same impulse conversion factor (1 impulse = x μw sec/cm^2) for all solar heights seems accidental. Apparently it depends principally upon the spectral transmission of the glass enclosure, the spectral response of the photosensitive surface, and the response with angle of incidence of the exciting radiation upon the receiver.

It is shown, beginning on page 30, that with the Mg-phototubes (which had a characteristic response with respect to the wavelength of the exciting radiation, and a response with angle of incidence that coincided closely with that predicted by the cosine law) the conversion factor varied with the solar height (see fig. 3 of [4]). Hence, in calculating the herein-described data, obtained with phototubes Mg-2 and Mg-41-1, a different conversion factor (microwatt-seconds per square centimeter) had to be applied to the impulses received during each half-hour of the day. On the other hand, for a number of the Zr-phototubes, particularly Zr-15, used in the present investigation, within the experimental errors of making the calibration the same conversion factor was applicable to all the impulses recorded throughout the day. It was therefore a simple matter to deduct the printed morning reading from the evening reading, thus securing the total number of impulses and, by applying a single conversion factor, the total amount of biologically effective ultraviolet solar and sky radiation per day. Obviously, with such cells and impulse counters in operation it would not be necessary to tabulate the data oftener than once per week or month.

1. DESCRIPTION OF THE ULTRAVIOLET METERS

Two types of ultraviolet intensity meters, in their mounting, were investigated. Unforeseen difficulties in the development of the device prevented an intercomparison of these meters with a proposed third type of ultraviolet meter [30].

In the first type of mounting shown in figure 2, the Mg-phototube (fig. 3 of [3]) is cemented into a moisture-proof, cylindrical brass housing. The auxiliary apparatus, consisting of a variable air condenser, a suitable resistance, and two grid-glow (trigger) tubes, WL

759 [5] (one for constant use, the other for infrequent use to check the constancy of the former and to replace it if necessary) is mounted on a chassis within the metal housing. The trigger tubes were interchanged by means of a switch that was connected (through a moisture-proof joint) to a lever arm beneath the housing, shown at *L* in figure 2. During the 10 months that the constancy of the trigger tubes was under observation, no systematic change (if any) in the discharge rate greater than 2 percent was observed. The question of constancy of the discharge rate, therefore, needs no further discussion. Our observations are in agreement with the claims of the manufacturer, that, barring defective samples, there is no deterioration in the discharge rate with usage of these trigger tubes.

The variable air condenser was connected with a shockproof metal rod that extended through the bottom of the container. After adjusting the capacitance of the condenser to produce 15 or 20 discharges ("impulses", "clicks") per minute under maximum ultraviolet irradiation of the phototube, the end of the rod was covered with an airtight metal cap, which remained undisturbed during the 18 months that this phototube, Mg–41–1, was under observation. The interior of the metal housing was kept dry by means of anhydrous $CaSO_4$ ("indicating") in a glass container, *D*, figure 2. The joints, *J*, in the housing were covered with aluminum paint. If any moisture entered the housing, it was not sufficient to change the blue color of the indicator during the 2 years that elapsed after the device was assembled.

This part of the apparatus was securely mounted on the parapet of the roof of a four-story building, which permitted exposure of the photoelectric receiver to the whole sky.

The construction of four of these phototubes in their mountings was undertaken by R. J. Cashman for the Council on Physical Therapy [1]—two for use at his station (Evanston, Ill.) and two for use at the National Bureau of Standards as primary standards and for comparison of ultraviolet intensities at these two stations. Unfortunately, this program was interrupted by military matters.

In view of the novelty of the phenomenon, it is of interest to record a type of deterioration that occurred in phototube Mg–41–1 (fig. 2), which had an excellent cosine response with angle of incidence and, at the beginning of the measurements, was a promising primary standard. In this type of photoelectric cell the anode usually consists of two bow-shaped metal wires at right angles to each other (see fig. 3). In order to determine the effect (if any) of the shape of the anode upon the critical voltage in this particular cell (fig. 2), the anode consisted of a flat grid of six wires (three at right angles to each other) parallel with and about 8 mm above the plane of the photosensitive cathode, *R*.

After being in operation continuously for 14 months, in July 1942 the impulse rate of this cell began to increase, presumably as a result of an increase in sensitivity in the long wavelengths. A small (3 mm) spot, with a metallic luster, developed on the top of the glass dome and a faintly brownish-colored spot appeared on the side, on a level with the cathode. In the course of the next 3 months the photosensitivity increased by 26 percent, and the dome showed six faintly brownish-colored bands (three at right angles to each other), each

about 3 mm in width, directly over the six fine wires forming the anode. Moreover, vertically above the 9 intersections of the wires, and over most of the 12 right-angled bends in these wires, these bands of discoloration were darker and rectangular or triangular in outline. The intersection of the two dark bands in the center of the glass dome was rectangular in outline, and within this rectangular area of discoloration was a circular darker-colored area. This central dark area, as well as several others, and part of the adjacent uncolored glass was covered with minute (0.01 mm diameter, some circular) dark specks—apparently the beginning of a disintegration of the glass by electron bombardment.

In the second type of mounting investigated the auxiliary apparatus (consisting of a condenser of suitable capacitance and a grid-glow tube) was mounted in an evacuated glass tube sealed to the Zr-phototube [8].

The flat receiver [3], which is about 35 mm in diameter, is a modification of the semicylindric photosensitive receiver of Ti [5] originally used in this type of photoelectric cell [8], (see fig. 2 of [9] and fig. 1 of [10]).

The complete tube, which is about 6 cm in diameter and about 40 cm long, is mounted in a suitable metal housing, with only the top part exposed, as shown in figure 3. The leveling, which need not be very accurate, is accomplished by means of suitable wooden blocks placed under the supports, which are securely attached to the parapet of the roof.

In the early models of Zr-phototubes employing this type of construction the accumulation of electric charges on the interior of the glass dome (of high-silica glass) suppressed the emission of electrons from the photosensitive receiver. This suppression of electron emission was erratic, sometimes continuing for 2 to 3 hours in the early forenoon. It was partially remedied by Stair by placing a guard ring around the outside, at the level of the receiver, and connecting it (through a 1-megohm resistance) with the positive line to the phototube. In some of the Mg-phototubes (see fig. 3 of [3]), the guard ring of evaporated metal or of Aquadac (colloidal carbon) was on the interior of the phototube. It is probable that the glass (Corning No. 972) used in the Mg-phototubes [3] dissipated the electric charges more readily than the high-silica glass used in the Zr-phototubes.

To eliminate the effect of electric charges, in the most recent models of Zr-phototubes the photosensitive receiver is inclosed in a larger glass bulb (about 8 cm. in diameter) than previously employed, thereby practically doubling the distance of the receiver from the glass dome. In this model, wiping the glass bulb has no effect upon the photoelectric emission. Although the external guard ring is retained, in view of the fact that its use on the smaller glass bulbs did not entirely prevent suppression of electron emission, by electric charges when the glass was wiped, it would appear that the solution of this problem is in the use of a larger-sized glass bulb. Another improvement consists in placing a small drainage tube at the bottom of the phototube, so that if moisture seeps in at the top it cannot accumulate and short-circuit the lead-in wires, as was experienced in the early models.

2. STANDARDIZATION OF THE ULTRAVIOLET METERS

For use as a primary standard of measurement, in absolute value, of the biologically effective component of ultraviolet solar and sky radiation incident on a horizontal plane, the logical procedure would be to standardize the radiometer in terms of homogeneous radiation of wavelength 2967 A, as previously proposed [9, 11] for instruments used in measuring solar radiation at normal incidence. Thus far, however, this procedure has not been practicable for either type of instrument. Hence, in connection with the use of instruments for measuring solar and sky radiation incident on a horizontal plane, two methods of standardization [4] were undertaken: (a) by calibration against a standard of ultraviolet radiation [11], and (b) by calibration against an ultraviolet-intensity meter [3, 9] that measures radiation incident normal to the photoelectric receiver [2]. The latter was calibrated against a standard of ultraviolet radiation [11] and gave ultraviolet solar-radiation intensities, of wavelengths shorter than 3132 A, in close agreement with measurements made with a balanced thermopile [12, 13, 14], which was calibrated against a standard of thermal radiation [15]. Since the measurements made with the balanced thermopile (see figs. 4, 5, and 6 of [12]) were in good agreement with those obtained with a single thermocouple receiver that had been calibrated in absolute value by means of a standard pyrheliometer, the above method (b) of calibration is based upon three standardized sources of radiation—the sun [12, 28], a standard of thermal radiation [15], and a standard of ultraviolet radiation [11].

In a recent paper on this subject (p. 437 and 443 of [2], also p. 323 of [14]), it was noted that the level of all the measurements may be uniformly too high or too low, primarily because of the difficulty in determining the spectral-energy distribution in the biologically effective band of ultraviolet solar radiation, of wavelengths 3132 A and shorter, and, hence, the uncertainty of the factor used in calculating the data. The accuracy attainable in the measurement of the biologically effective component of ultraviolet solar radiation, in absolute value, is therefore somewhat of a conjecture. However, as noted elsewhere [14, 16] and from the herein-described erythema tests (which are in accord with previous tests [12, 13]), the good agreement in the measurements of the biologically effective component of ultraviolet solar radiation of wavelengths 3132 A and shorter, obtained with spectrally nonselective thermopiles and with wavelength selective radiometers differing greatly in range of spectral photoelectric response, appears to be real and not the result of a fortuitous combination of factors, including (a) the spectral responses of the photoelectric cells [2, 31, 32, 34], (b) the spectral transmissions of the filters, and (c) the transmissions of the integrated ultraviolet solar radiation through the various filters [10, 33]. Hence, although the production and calibration of a primary standard ultraviolet radiometer is incomplete, it is believed that the degree of accuracy attained in the calibration of the instruments used in the present investigation is as high as warranted by the constancy of the behavior of the photoelectric cells now available and the irregularity of meteorological conditions experienced from day to day.

Because of the exigency of other activities and the lack of time to work out the factors involved in the above-mentioned method (a), it seemed best, at the time, to standardize the ultraviolet meters (which

are easily disturbed by handling) by a method that permits a calibration of the instruments in place, undisturbed as used in practice. This method, (b), in which the various factors have been worked out during the past 10 years, consists in measuring the ultraviolet solar intensity in absolute value ($\mu w/cm^2$) incident normally, with a standard ultraviolet intensity meter [9, 2]. Simultaneously, a measurement was obtained of the combined ultraviolet solar and sky radiation, and (by intercepting the direct solar beam with an occulting screen) of only the sky radiation incident on the horizontal photocell receiver (see p. 155 of [3]).

This is the procedure of the United States Weather Bureau in calibrating pyrheliometers used for measuring the total sky and solar radiation incident on a horizontal plane [26]. It places the uncertainty of the calibration upon the pyrheliometer designed for measuring radiation at normal incidence, and, as above noted, in the case of the nonselective pyrheliometer there is half a century of research on the accuracy attainable. In the case of the spectrally selective radiometer (photocell), because of the above-noted uncertainty in the energy distribution in the biologically effective band of ultraviolet solar radiation, high accuracy in the absolute values is not yet attainable (p. 443 of [2]).

The occulting screens used with the photoelectric cells were blackened rubber balls, 30 mm in diameter, for shadowing the receivers, 25 mm in diameter, and blackened spherical balls of balsa wood, 43 mm in diameter, for shadowing the receivers, 38 mm in diameter. By actual trial it was found that balls 2 mm larger, and smaller, in diameter had no effect upon the impulse rate ("clicks"), showing that radiometrically as well as visually the shadowing from the direct solar rays was complete. These occulting balls were attached to a thin wooden rod, about 50 cm long, that was mounted on a polar axis, attached at *P* in figure 3. They were about 60 cm from the receiver.

For convenience in securing an accurate time scale, the impulses were recorded by means of a graphic milliammeter (see fig. 4 of RP1075 [17a]) operated by a synchronous motor. For this purpose the graphic recorder was temporarily connected in parallel (at T, fig. 1) with the impulse counter and printing recorder.

The electric discharges (impulses) from the ultraviolet meter produced a series of galvanometer deflections (ink lines about 5 mm long) on the recording sheet. The intervals between these ink lines (impulses) were, of course, longer during the period of shadowing of the receiver than during the period of exposure to the sun and the sky. Except when the altitude of the sun was low, a fixed schedule of recording was usually followed: (a) an exposure of the phototube for 2 min to the sun and sky, followed (b) by a 3-min interval of shadowing of the receiver from direct sunlight, i. e., exposure to the sky. This schedule was repeated every 5 min, in succession, for 1 to 5 hr. The distance between the 1-min intervals ruled on the recording paper (see fig. 4 of RP1075 [17a])was 19.2 mm. By measuring the distance recorded between 5 to 15 lines (impulses), recorded in the 2- to 3-min intervals allotted to each set of observations, a high precision was attained in the measurement of the impulse rate, i. e., the ultraviolet radiant flux from the sky and from the sun.

Provided with an accurate time scale, which was recorded with the graphic milliammeter, on deducting the ultraviolet sky radiation from

the total (sun+sky), the ratio of intensities (impulses per unit time—the fractional impulse per second in the instruments used) of sky radiation to solar radiation incident on a horizontal plane is easily determined. As shown in figure 4, the biologically effective component of ultraviolet radiation from the whole (cloudless) sky incident upon a horizontal surface depends upon the solar height (air mass traversed by the direct solar rays) and upon atmospheric turbidity. Even during the clearest days, at a practically sea-level station (Washington), the ultraviolet component of sky radiation is rarely less than (and usually it is 2 to 5 times greater than) that of direct solar radiation (see fig. 4).

From the measurement of the ultraviolet solar radiation incident normally (reduced to incidence on a horizontal plane [29]) and the ratio of ultraviolet sky radiation to solar radiation, the total solar and sky radiation incident on a horizontal plane is easily determined.

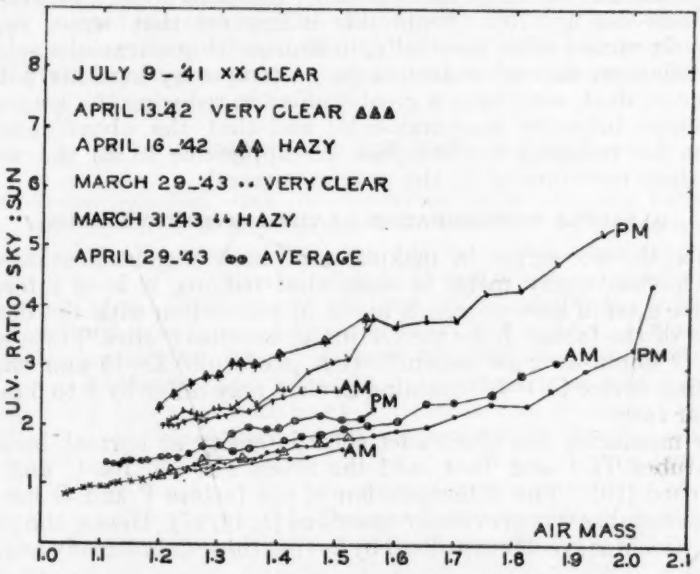

FIGURE 4.—*Measurements of ratios of ultraviolet sky and solar radiation incident on a horizontal plane.*

From the measurement of the total ultraviolet solar and sky radiation, incident on a horizontal plane, the factor for converting an impulse into energy units (μw sec/cm^2, the ultraviolet solar energy effective in charging the condenser to produce one "click") is derived. A typical set of solar and sky radiation measurements and the derivation of a conversion factor are given at the end of this chapter.

As noted in the preceding paper [2], the measurements of ultraviolet solar radiation incident normally upon wavelength-selective and nonselective radiometers are in good agreement. Hence, the present measurements are made consistently on the same basis and can be revised if eventually such a revision is required.

It is to be noted that these cal brations were made on the clearest days. The factors for reducing the impulses are, therefore, average

values for clear-weather conditions. Naturally, the question arises regarding the factors for overcast skies. From earlier studies [10] it appears that fog and clouds of water vapor reduce the incident spectral ultraviolet radiation relatively nonselectively, whereas dust and smoke behave like an opaque screen.

An intercomparison of Zr-phototubes differing (a) in intrinsic sensitivity, (b) in response with angle of incidence of irradiation ("cosine response"), and (c) in range of spectral response, sometimes showed short-period variations in the ratios of impulses recorded that appeared to be attributable to variations in transparency of ozone in the stratosphere. However, based upon an extensive intercomparison of phototubes Zr-53, Zr-15, and Mg-3, differing in sensitivity by, roughly, 1:2:3, the ratio of the total impulses per day (1:2.17:2.80) was the same within 2 to 3 percent on cloudy days (e. g., July 8, 1943, 1,428 impulses with phototube Zr-15—see fig. 10) as on fairly clear days that produced over three times as many impulses (June 26, 1943, 4,640 impulses—see fig. 10). From this it appears that water vapor is relatively nonselective spectrally, in transmitting ultraviolet solar and sky radiation; that other factors (e. g., temporary local air pollution by smoke, dust, etc.) have a greater effect in reducing the accuracy of ultraviolet intensity measurements; and that the above-mentioned factors for reducing the impulses are applicable to all the weather conditions encountered in the present research.

(a) SAMPLE DETERMINATION OF THE CONVERSION FACTOR, *I*

Since the procedure in making a primary standardization of an ultraviolet-intensity meter is somewhat tedious, it is of interest to describe a set of measurements made in connection with the determination of the factor, I, for converting an impulse ("click") into energy units (1 impulse$=x$ μw sec/cm^2) with phototube Zr–15 and impulse-counting device C41–4—counting devices may differ by 3 to 5 percent in their rate.

For measuring the ultraviolet solar intensity at normal incidence, phototubes Ti–1 and Ti–4, and the filters Cx, Ni, Ba–1, and Ba–3 were used [10]. The determination of the factors P and G for these two phototubes was previously described [2, 14, 17]. Hence, the present calibration was greatly expedited by having these data already available.

The following is a partial transcription of the data obtained at 11:20 to 11:27 a. m. on April 29, 1943.

I. Sun, normal incidence; phototube Ti–4. Time 11:22 to 11:27 a. m. Air mass, $m=1.12$; solar height 63.5° (sine$=0.895$). Observed solar intensity$=62.2$ μw/cm^2;$=55.7\mu$w/m^2 on a horizontal plane.

II. Sun+sky, incident on a horizontal plane; phototube Zr—15. Time 11:20 to 11:22 a. m. Average of 10 and of 15 clicks; 1 click$=1.90$ mm on the recorder chart (1 mm$=3.16$ sec.); same value at 11:25 to 11:27 a. m., 1 click in ($1.90\times3.16=$) 6.01 sec (0.1665 click in 1 sec).

III. Sky radiation; 11:22 to 11:25 a. m. Average of 10 and of 15 clicks; 1 click$=$ 3.305 mm on recorder chart (1 mm$=3.16$ sec). 1 click in 10.44 sec (0.0958 click in 1 sec).

Solar radiation produced ($0.1665-0.0958=$) 0.0707 click in 1 sec.
Ratio of sky to solar radiation ($0.0958\div0.0707=$) 1.355.
Total solar+sky radiation [$55.7+(1.355\times55.7=$] 131.2μw/cm^2.
Factor, $I=131.2\times6.01=788$ μw/sec/cm^2.

In connection with the foregoing record of observations, it is relevant to note that on April 29, 1943, in the forenoon, upper-air conditions underwent sudden variations; from "clear blue, small

white corona" to a few "thin cirrus-fracto clouds" that disappeared in a few minutes. From 8:57 to 9:10 a. m. (air mass, $m=1.51$ to 1.44) a faint "sun dog" was visible, followed by murkiness and an occasional thin fracto cloud. In spite of these variations, the ratios for the integrated ultraviolet of the whole sky relative to the direct solar radiation are fairly uniform—see figure 4.

As shown in a previous paper (fig. 3 of [4]), the factor for converting impulses into ultraviolet intensities, measured with phototube Mg–41–1 varied with the solar height. In that illustration the calibration pertains to the wavelength range of 3200 A and shorter. For the herein-used spectral range of 3132 A and shorter, the factor is reduced by about one-half at air mass 1.1 and decreases practically linearly with increase in air mass.

Using ultraviolet meter Zr–15, the factor, I, did not vary with the (air mass) solar height, the average value being 1 impulse=780 μw sec/cm^2. This fortunate circumstance simplified the calculations, for it was necessary simply to multiply the total impulses per day by the factor I, instead of summing the values recorded each half hour. As noted in the beginning of this chapter, in some of the Eppley pyrheliometers the same factor (millivolts per gram-calory) obtains throughout the day.

III. DISCUSSION OF THE DATA

The herein-described data on ultraviolet solar and sky radiation of wave lengths 3132 A and shorter were obtained with instruments mounted on the parapet of the roof of the South Building of the National Bureau of Standards, latitude 38° 56.5′ N, longitude 77°4′ W, elevation about 410 ft above sea level. The locality is practically residential, in the northwest section of Washington, D. C. There are no factories, and most of the atmospheric pollution (by the combustion products of automobiles, incinerators, oil burners, and coal furnaces in office buildings and apartment houses) occurs southeast of the Bureau. The prevailing wind is from the west or northwest quadrant, where the suburban Maryland villages (no factories) are few, and there is no dense smoke. Only on very rare occasions, such as mentioned on p. 953 and 964 of [28], is a dense, low-lying, stratum of smoke and finely divided particles of dust carried over this locality by an east wind. The stratum of smoke from railroad engines, office apartment buildings, etc., that is visible some 4 miles to the southeast, may intercept direct solar radiation in the early morning in winter. No doubt there is a pall of atmospheric pollution over this city, similar to that observable on the clearest days, low on the north-northeast horizon, presumably over the city of Baltimore, some 30 miles distant.

On the clearest days in the winter and spring the wind may be from the north instead of the northwest, and a light "smoke" (dry coal dust) that occasionally issues from a tall chimney, situated due north, may be blown over the photoelectric receivers. This, however, is of infrequent occurrence and of short duration. Hence, considered as a whole, the herein presented data are representative of localities, in this latitude, relatively free from local atmospheric pollution and having similar meteorological conditions.

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1. EFFECT OF CLOUDS

It is well recognized that the amount of ultraviolet solar radiation reaching any spot on the earth's surface is determined by the amount of ozone in the stratosphere; also by local atmospheric pollution (by smoke and dust) and by the distribution of clouds in the lower atmosphere.

In the Zr-phototubes the response is somewhat higher than predicted by the cosine law, with angle of incidence. Hence, under

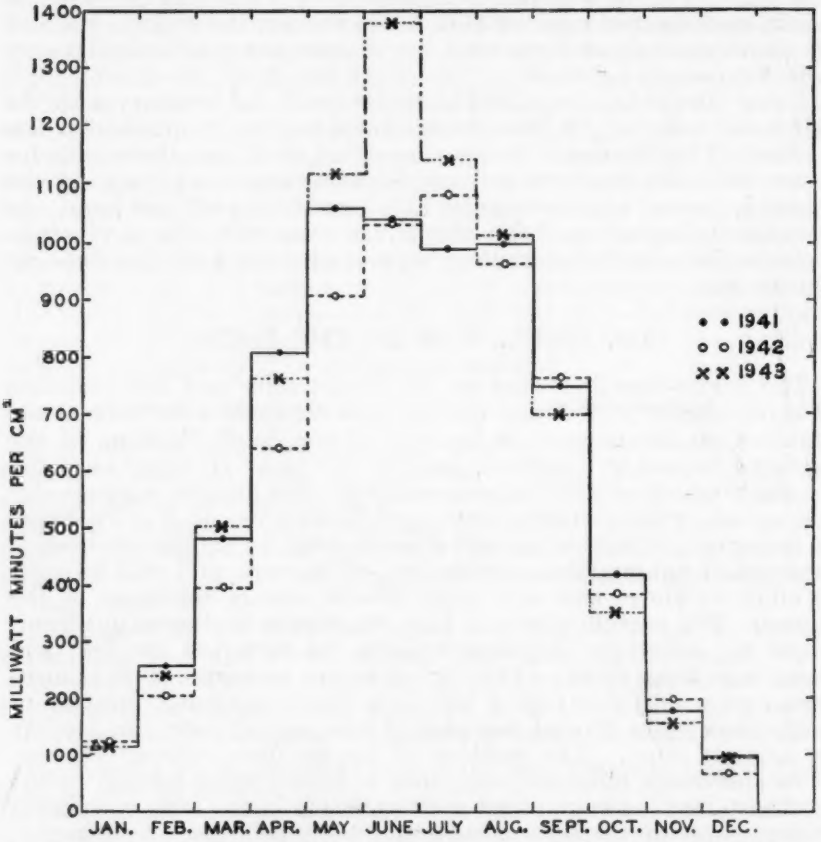

FIGURE 5.—*Monthly totals of biologically effective ultraviolet solar and sky radiation, in milliwatt minutes per square centimeter, incident on a horizontal plane, in Washington, D. C., during the years 1941 to 1943, inclusive (also Jan. 1944, ΔΔ).*

These data were calculated from observations depicted in figures 8, 9, and 10.

certain cloud distributions the number of impulses produced by ultraviolet radiation may be greater than expected. This, however, does not greatly affect the average values, and it does not explain the high values obtained with certain kinds of cloud formations, viz, small fleecy clouds, near but not in the line of sight with the sun, as noted by other observers [19, 20, 22].

For example, on June 28, 1943, which was listed as "hot and partly cloudy", an exceptionally large number of impulses (4,858) was re-

recorded (see fig. 10). There was a high wind and large, rapidly moving fracto-cumulus clouds. The intervening sky was exceptionally clear, blue (not "contrast blue"), and free from turbidity. At the noon-hour the impulses were 14 to 15 per min—an exceptionally high rate, even on the clearest days. In contrast, on June 4, which was listed "clear with a few thin cirrus-fracto clouds at 10 a. m. and 1 p. m.", the total number of impulses (4,942) recorded was not conspicuously larger, (see fig. 10), than noted above for June 28. The length of day and the air masses traversed by the direct solar rays were practically the same on these two dates. Apparently the fracto-cumulus clouds reflected an appreciable amount of ultraviolet radiation.

The month of June 1943 was conspicuous for low precipitation, but numerous days of partial cloudiness—fracto-cumulus, alt-cumulus, and cirro-cumulus. Nevertheless, the total amount of ultraviolet received is exceptionally large (see fig. 5). In contrast, in the month of July 1943, which also had low precipitation and much cloudiness of the nimbus type, the total ultraviolet received is much

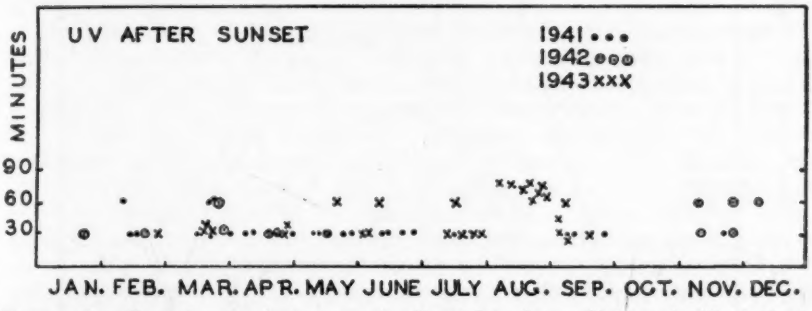

FIGURE 6.—*Conspicuous instances of ultraviolet sky radiation incident during evening twilight—time in minutes after sunset.*

lower (see fig. 5). In fact, during the first week in July the total incident ultraviolet solar and sky radiation was only about 60 percent of that of the last week in June.

As noted in previous papers [2], the atmospheric transparency to ultraviolet radiation is greater in the fall than in the spring; also greater in the afternoon than in the forenoon. This was repeatedly observed in the present measurements when the recorder registered impulses at sunset and 30 to 60 min thereafter. As shown in figure 6, this occurred in different years. For example, in 1943 there seemed to be a large number in the latter part of August (an excessively dry month) and the first part of September. The nonoccurrence in October is probably fortuitous.

Evidently, these impulses were produced by ultraviolet solar radiation that entered the upper atmosphere and was reflected downward from near the zenith upon the ultraviolet meter [37]. The intensity, of course, is very low, as indicated by the slow charging of the condenser to a critical voltage. For example, on December 6, 1942 (cloudy day, sky clear in the evening, sunset at about 4:45 p. m.) no impulses were recorded between 4:15 p. m. and 5:45 p. m. and only

1 impulse at 6 p. m., which was produced by the charge accumulated during the interval beginning half an hour before sunset and ending about an hour after sunset. Similarly, with the group observed in the latter part of August 1943—see figure 6. From earlier (negative) tests made during moonlight nights [4b] it appears highly improbable that these occasional impulses were caused by artifical sources but were due to a partial charging of the condenser by upper-air ultraviolet sky radiation, before sunset, and the completion of the charging, to the critical voltage, during twilight on evenings when the sky was exceptionally clear.

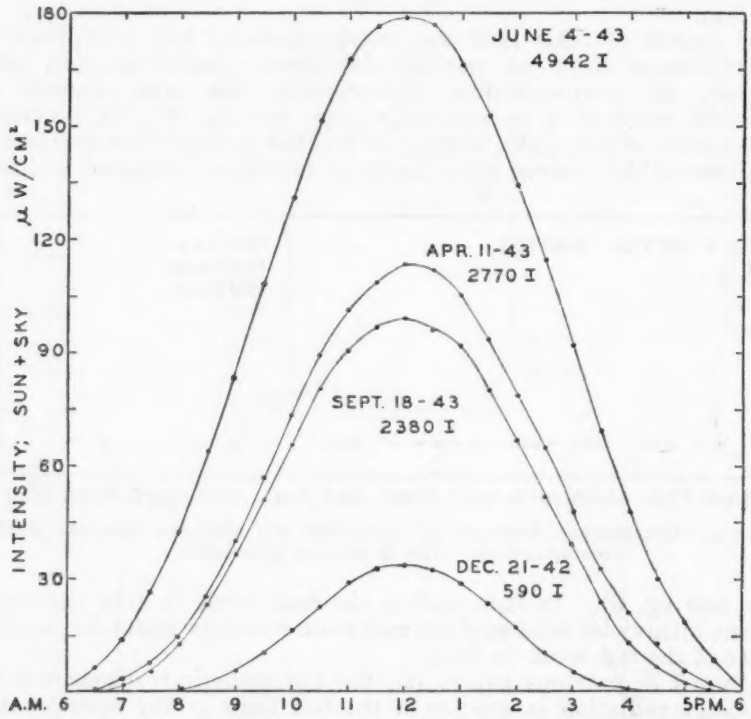

FIGURE 7.—*Daily and seasonal variation in intensities of ultraviolet solar and sky radiation incident on a horizontal plane, in microwatts per square centimeter (also total impulses, I), observed on four very clear days in Washington, D. C.*
Measurements made with phototube Zr-15.

2. SUMMARY OF MEASUREMENTS

In previous publications [2, 14], it is shown that on the clearest days, at the noon hour, in Washington, the ultraviolet solar intensity of wavelengths 3132A and shorter at normal incidence ranges from about 75μw/cm^2 in June to one-sixth this value in December. For comparison, in figure 7 are depicted the average intensities of solar and sky radiation incident on a horizontal plane on four very clear days in Washington. These values are calculated from the printed records of impulses received during half-hour intervals. The intensities of combined solar and sky radiation, incident on a horizontal plane,

at midday, ranged from about 180μw/cm^2 on a very clear day in June to 33μw/cm^2 (about one-sixth the summer value) in December [4].

From the foregoing paragraph it is interesting to note that, for these two seasons, the ratio of intensities of ultraviolet solar radiation at normal incidence and of total ultraviolet solar and sky radiation incident on a horizontal plane are not conspicuously different. This of course might be expected. As shown in figure 4, for low solar altitudes the sky contributes most of the ultraviolet incident on a horizontal plane. Only on the clearest days and for air masses less than $m=1.1$, at a sea-level station, is the intensity of the directly incident, biologically effective ultraviolet solar radiation equal to, or greater than, that of the diffusely reflected ultraviolet radiation from the whole sky incident on a horizontal surface.

In these illustrations the numbers (590 I in fig. 7; also fig. 8, etc.) are the total impulses recorded during the day. Using the calibration (conversion) factor, 1 impulse=780 μw/cm^2, the daily totals, in energy units, ranged from 7.68 mw min/cm^2 (mw=milliwatt) on December 21, 1942 to 64.3 mw min/cm^2 on June 4, 1943—see figure 5 for monthly totals.

In figures 8, 9, and 10 are depicted the total daily impulses recorded and, hence, measurements of the total ultraviolet solar and skyradiation incident at the Washington station during the period beginning February 1, 1941 and continuing without interruption through December, 1943. In figure 10 (Zr-15—different sensitivity) the scale of ordinates is different from that of figures 8 and 9. This is eliminated by the conversion factor, which is different for each photoelectric cell used in this research. It has already been noted that unusually high values of ultraviolet intensities were recorded on certain cloudy days. No doubt interesting bioclimatological information will be obtained when such measurements can be continued systematically over a long period. For example, September 29, 1943 was a clear day, and, contrary to expectation, a relatively low number (1,157) of impulses was recorded. The barometer had been high for 2 days and continued high until noon the following day. This usually indicates a low ozone concentration in the stratosphere. Apparently there was already (a "cold front"), an inflow of polar air, producing an increase in ozone concentration in the stratosphere preceding the decrease in barometric pressure [36] and the cloudy weather that occurred the following day.

Supplementing the observations depicted in figures 8, 9, and 10, the total impulses per month were converted into energy (e. g., for Zr-15, 1 impulse=780 μw sec/cm^2). These monthly values are shown in figure 5. As is to be expected, the high values recorded in April, August, and September 1941, and in June, July, and August 1943, are evident from an inspection of the large clear areas under the graphs in figures 8 and 10.

Considering the fact that it does not require a great difference in cloudiness to affect the daily and monthly totals, especially in the summer months, the monthly totals for these 3 years are remarkably close in magnitude, except for the months of May, June, and July 1943. With an excessively large number of days with temperatures above 33° C (90° F; the largest number of days in half a century) and a low precipitation during June, July, and August, the much higher values of the integrated ultraviolet intensities in 1943 than observed

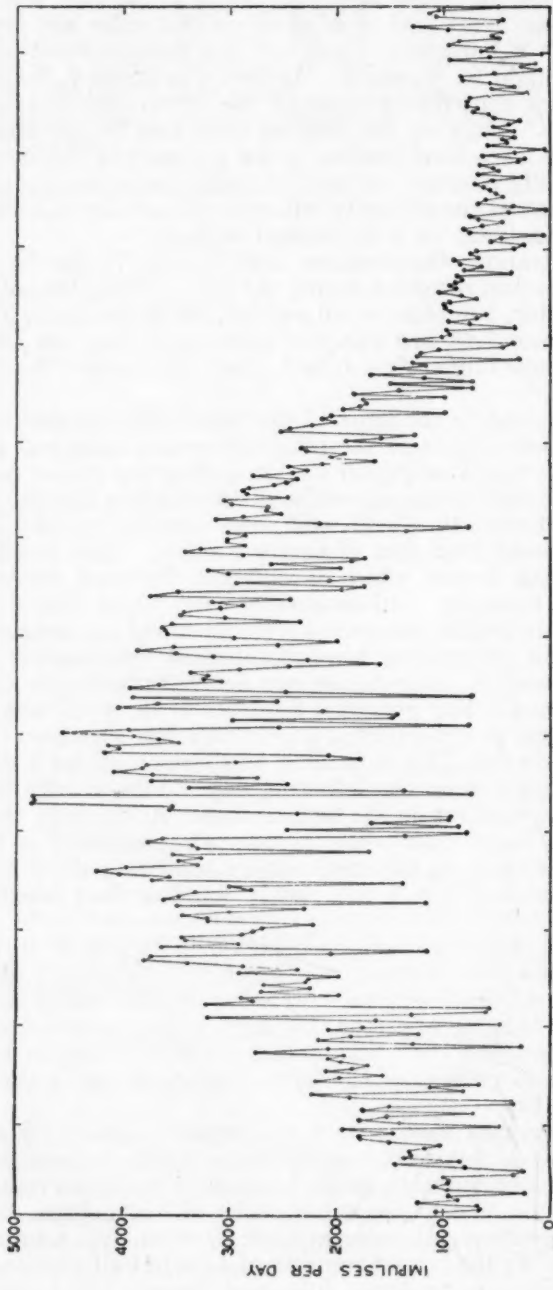

FIGURE 8.—*Impulses per day, and hence, a relative measurement of the total integrated daily amount of biologically effective ultraviolet solar and sky radiation incident in Washington, D. C., in 1941.*

Measurements with Mg-2, (February to June) and with Mg-41-1 phototubes.

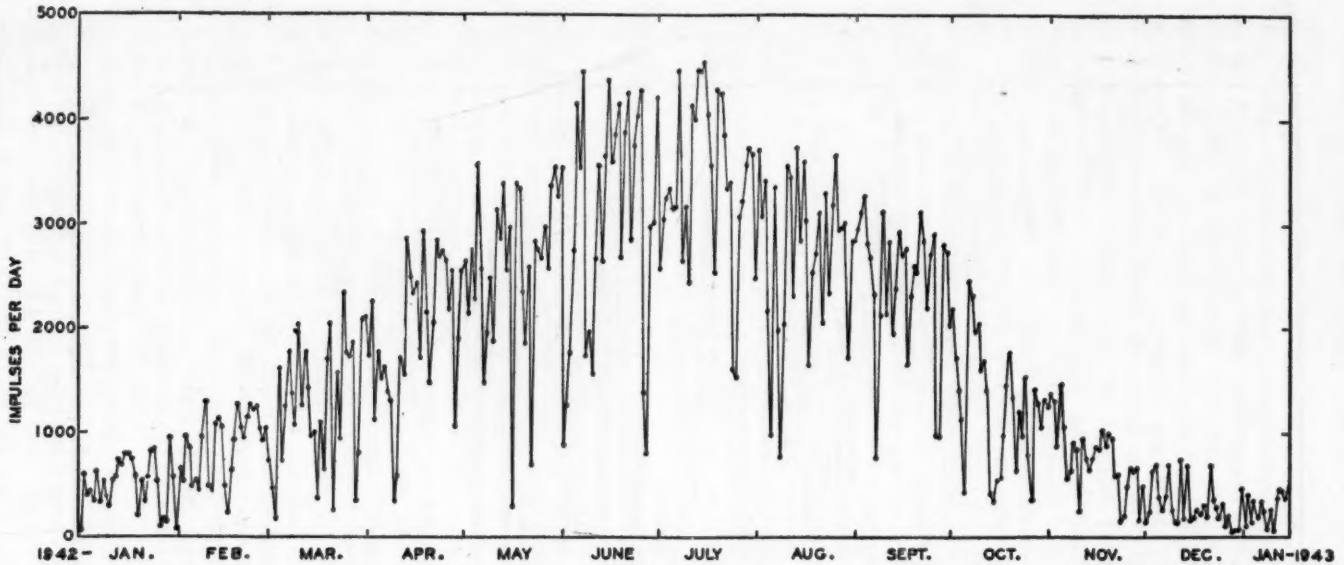

FIGURE 9.—*Impulses per day, and hence, a relative measurement of the total integrated daily amount of biologically effective ultraviolet solar and sky radiation incident in Washington, D. C., in 1942.*

Measurements with Mg-41-1, and with Zr-15 (in November and December).

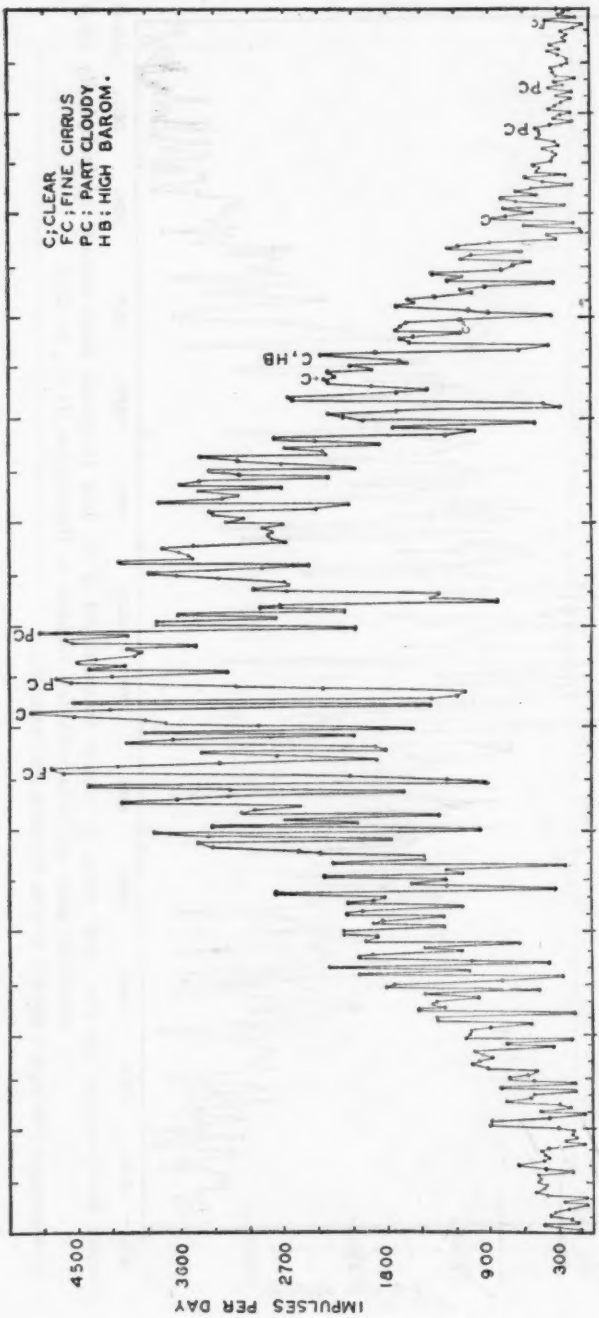

FIGURE 10.—*Impulses per day, and hence, a relative measurement of the total integrated daily amount of biologically effective ultraviolet solar and sky radiation incident in Washington, D. C., in 1943.*

Measurements with phototube Zr-15.

during the preceding 2 years are easily accounted for on the basis of clearer weather.

Because of the impossibility of obtaining delivery of an adequate supply of good photoelectric cells for a continuous intercomparison of performance of a group of cells, the calibration of the ultraviolet intensity meters used in the present research was made by direct standardization of each instrument, as above described.

There is, therefore, no doubt a small uncertainty in the intercomparison of the monthly data obtained during different years. However, the values have been reduced by the factor 60,000 (to milliwatt-minutes). Hence, statistically and climatologically, the monthly sums, shown graphically in figure 5, can be regarded satisfactory for present purposes. Similar large variations in the monthly values, extending over an interval of 4 years, are shown in figure 3 of [22]. In fact, from the records of the great variations in the monthly averages of total solar radiation, similar variations in the ultraviolet component of solar and sky radiation are to be expected.

A conspicuous feature in figure 5 is the great difference in the seasonal values of ultraviolet solar and sky radiation, with much higher values in the autumn. This great difference is especially noticeable in the months of comparable solar heights, March and September, April and August, February and October, and January and November. As noted in a previous paper [2], this is due to the presence of a less amount of ozone in the stratosphere (hence, a greater amount of incident ultraviolet solar radiation) in the autumn than in the spring.

IV. ERYTHEMA TESTS WITH ULTRAVIOLET SOLAR AND SKY RADIATION

In previous papers [12, 13] data are given on the erythematogenic efficiency of heterogeneous ultraviolet radiation from the sun and from artificial sources of radiation, at normal incidence, using homogeneous radiation of wavelength 2967 A as a comparison standard. It was therefore of interest to obtain measurements of the erythematogenic effectiveness of ultraviolet solar and sky radiation incident on a horizontal plane. If there is a marked difference in the spectral composition of sky and direct solar radiation or in the calibration of these two types of ultraviolet-intensity meters, it should be observable in the total energy required to produce a minimum perceptible erythema, when using a combination in which the sky radiation is 2 to 3 times the amount of solar radiation. From the herein-described erythema tests apparently there is no marked difference in the spectral composition of sky and solar radiation. Hence, no attempt was made to prolong this part of the investigation, using the refinements of comparison with the standard of homogeneous radiation of wavelength 2967 A described in previous papers [12, 13].

In making these erythemal exposure tests the untanned part of the inner side of the upper arm was covered with a cardboard shield perforated with a row of seven holes, each about 4.5 mm in diameter, as shown in figures 1 and 2 of [27]. A sliding cover of white cardboard permitted individual exposures ranging from 8 to 90 min. The rest of the arm was covered with a white cloth to prevent sunburn and tanning.

In making the exposures to solar and sky radiation the observer faced south, with the arm resting on a support placed on the parapet of the roof, a short distance from the ultraviolet-intensity meter. The arm was extended horizontally, on a level with the shoulder, and, since the amount of ultraviolet sky radiation incident from levels near the horizon is extremely small [22], no correction was made for shadowing by the head.

Test No. 1.—June 19, 1943; sky cloudless, except on the east horizon; hot, very light breeze; between 10:50 (Eastern Standard Time; air mass, $m=1.07$) and 11:23 a. m., seven exposures were made of, respectively, 10, 15, 20, 23, 26, 29, and 33 min.

All but the first exposure (10 min.) showed erythema that continued for 24 hours and pigmentation that continued for several months. It was difficult to decide when erythema ceased and pigmentation began.

The ultraviolet intensity (u.v.Q) ranged from 150 to 158 μw/cm^2, average 155 μw/cm^2. The time for a minimum perceptible erythema (M. P. E.) was estimated at 13 to 14 min, or an expenditure of ($155\times13\times60\times10=$)1,210,000 to 1,300,000 ergs/cm^2. The recorder registered 175 impulses (1 impulse=780 μw sec/cm^2) in 15 min, indicating ($175\times780=$)136,500 μw sec/cm^2, or 1,365,000 ergs/cm^2 as a maximum to produce an M. P. E. These values are in good agreement with earlier determinations on the same subject (W. W. C. [12, 13]) exposed to solar radiation at normal incidence and to a small area of the surrounding sky radiation. In those erythema tests the exposures were made with a tall building as a background and tall trees at the sides and in the foreground, which excluded about 85 percent of the sky radiation. The ultraviolet solar radiation stimulus (88 to 90 μw/cm^2) was therefore 10 to 15 percent higher than the recently reported values (75 to 78 μw/cm^2 for normal incidence), which included but little sky radiation [2]. Two determinations (on June 2 and on July 22, 1931) required 1,728,000 and 1,056,000 ergs/cm^2, respectively, to produce an M. P. E., which is in as close agreement as can be expected in making the biological appraisal.

Test No. 2.—June 26, 1943; sky murky; very hot, very light or no breeze; between 10:45 and 11:03 a. m., seven exposures of, respectively, 8, 10, 11, 12, 13, 15, and 18 min thin cirrus, and a large fracto cloud near the sun at 10:53 to 10:58 a. m.

Exposures Nos. 3 (11 min) to 7 (18 min), inclusive, showed erythema (No. 7, very red) at 8 p. m. Exposures Nos. 5, 6, and 7 were still visible on the following evening. No. 7 (18 min) showed about the same pigmentation as No. 2 (15 min) of June 19. Three days later Nos. 5, 6, and 7 showed very faint pigmentation.

The u.v.Q ranged from 156 to 162 μw/cm^2, average 160 μw/cm^2. The time for an M. P. E. was estimated at 12 to 13 min, or an expenditure of 1,150,000 to 1,250,000 ergs/cm^2. The recorder registered 183 impluses in 15 min, indicating ($183\times780=$)142,600 μw sec/cm^2, or 1,426,000 ergs/cm^2 as a maximum.

These measurements were made during excessively hot weather, with air temperatures above 90° F (33° C). It is therefore an interesting question as to what effect excessive perspiration had upon erythema and particularly upon pigmentation, which seemed much less than in the 15-min exposure in the preceding test.

In these tests no measurements were made of the amount contributed by sky radiation. In the first test the sky was clear and the ratio of solar radiation to sky radiation was estimated to be about 1:1.3. In the second test the ratio of solar to sky radiation was probably 1:2.5, or perhaps higher for a short time when a large fracto cloud was near the sun. With variable sky conditions the advantage of using the photoelectric ultraviolet integrating device in measuring the ultraviolet radiation stimulus during the biological test is obvious.

Test No. 3.—July 1, 1943; cool, light breeze; at the beginning, sky clear, except on the horizon; between 12:22 p. m. and 12:41 p. m., seven exposures of, respectively, 8, 10, 12, 13, 14, 16, and 19 min.

At 9 p. m., exposures Nos. 5, 6, and 7 showed erythema (No. 5, very faint). The next day, Nos. 6 and 7 (16 and 19 min) showed slight pigmentation; exposure No. 5 (14 min), which happened to be over a vein, was indefinite. The time of exposure for an M. P. E. was estimated at 15 min.

During the first 8 min of the exposures, the sky was clear, and from the impulse recorder the average u.v.Q was 148 μw/cm^2, or a total of 711,000 ergs/cm^2. During the next 4 min, a small fracto formed and disappeared near the sun; and during the next 7 min, a larger, denser fracto cloud formed and moved to within a

few degrees from the sun. From the impulse recorder, the u.v.Q was estimated to be 140 μw/cm², or 589,000 ergs/cm² in 7 min, or a total of 1,300,000 ergs/cm² in 15 min. The maximum energy utilized in 16 min was 1,384,000 ergs/cm², with slight tanning. The pigmentation produced by the exposure of 19 min (1,634,000 ergs/cm²) was about as dark as that of the exposure of 18 min (1,730,000 ergs/cm²) in test No. 2. Apparently the light breeze and cooler air did not dry the skin sufficiently to require an appreciably larger doseage to produce an M. P. E.

Test No. 4.—July 16, 1943; warm, no breeze, skin moist; sky cloudless, except fine cirrus low on southwest horizon; between 10:51 and 11:10 a. m. (air mass, $m=1.09$) seven exposures of, respectively, 10, 12, 13, 14, 15, 17, and 19 min.

At 9 p. m., exposures Nos. 4 (14 min) to 7 showed light erythema that continued until noon the following day. The time of exposure for an M. P. E. was about 14 min. The average intensity of sun and sky radiation was 136 μw/cm², or a total of (136×840×10=)1,142,400 ergs/cm². The maximum energy utilized in the exposure for 16 min (skin red the following noon) was 1,304,000 ergs/cm².

With a cloudless sky the ratio of solar to sky radiation was probably 1:1.2. The total energy required to produce an M. P. E. was somewhat less than in all the preceding tests. It is, of course, impossible to decide how much of this decrease in energy was due to a clearer sky that transmitted a relatively greater amount of the biologically more effective ultraviolet of short wavelengths (average barometer, 754 mm, and presumably average ozone in the stratosphere [36]), and how much was caused by moisture on the skin, which facilitated penetration.

Test No. 5.—July 23, 1943; warm, light breeze, skin dry; sky clear, except a few fracto on southeast to southwest horizon; between 11:57 a. m. and 12:17 p. m. (air mass, $m=1.06$, barometer 754 mm); seven exposures of, respectively, 10, 12, 13, 14, 15, 17, and 20 min. The counter was set to record the impulses every minute. During the first 12 minutes, 129 impulses were recorded, representing an average intensity of 139 μw/cm²; the remainder of the time it was 143 μw/cm².

At 9 p. m., exposures Nos. 7 (20 min; red), 6, 5, 4, and 3 were visible. The erythema of exposure No. 5 was weaker than No. 4, and No. 3 was very faint. The following morning, exposures Nos. 7, 6, 5, and 4 (faint) were still visible, and by noon, Nos. 5 and 4 were very faint. Nos. 6 (17 min) and 7 were decidedly overexposed.

The energy used in producing an M. P. E. in 15 min (161 pulses; 1 impulse=7,800 ergs/cm²) was 1,256,000 ergs/cm². Granting that 16 min (172 impulses) was more nearly the time of exposure to produce an M. P. E., the energy used was (7,800×172=)1,342,000 ergs/cm². These values are more exact than in the preceding tests, from which they do not differ conspicuously.

Test No. 6.—September 18, 1943; cool light breeze, skin dry; sky cloudless, small corona; ratio of sky to solar radiation estimated to be 1:2; high barometer (765 mm)—probably low ozone; between 12:00 and 12:30 p. m. (air mass, $m=1.25$ to 1.26) seven exposures of, respectively, 14, 17, 19, 21, 24, 27 and 30 min. The intensity ranged from 93 to 96 μw/cm² (see fig. 7).

The interesting part of this test was that none of these exposures showed erythema, and only the exposures of 24, 27, and 30 min showed a faint pigmentation, although the energy involved ranged from 1,340,000 to 1,650,000 ergs. It is well established that the sensitivity of the skin depends upon one's physical condition. In this case, the subject concerned was suffering from the after effects of hay fever, which presumably affected the erythemal response.

Test No. 7.—September 28, 1943; warm, no breeze, skin moist; sky cloudless, at times murky, white corona; ratio of sky to solar radiation estimated to be 2.0 to 2.5; high barometer (760 mm) for 2 days—no doubt low ozone in stratosphere; between 11:55 a. m. and 1:25 p. m. (air mass, $m=1.34$ to 1.44) seven exposures of, respectively, 20, 30, 40, 50, 60, 75, and 90 min. The solar and sky intensity decreased from 68 μw/cm² at the start to 56 μw/cm² during the last quarter-hour. During the second through the fifth exposure the average u. v. Q was 60 μw/cm².

An interesting part of this test was that at the completion of the irradiation, exposures Nos. 7 to 2 (very faint) showed "heat" erythema. The next day, exposures Nos. 3 to 7, inclusive, were red and pigmented. Evidently the energy required to produce an M. P. E. was between exposure No. 2 (1,144,500 ergs/cm²) and exposure No. 3 (1,504,500 ergs/cm²), or about 1,300,000 ergs/cm², which is in good agreement with earlier tests with ultraviolet that has traversed through smaller air masses. Apparently, the photoelectric response and the erythemal response do not differ greatly in their integration of the ultraviolet transmitted through air masses $m=1.05$ to $m=1.5$.

Probably the most conspicuous result of this series of erythema tests is the observation that the total biologically effective ultraviolet energy in sky and solar radiation incident on a horizontal plane required to produce an M. P. E. is practically the same as that of ultraviolet solar radiation at normal incidence. This seems to indicate that, in spite of the above-mentioned uncertainties in the ultraviolet spectral-energy distribution of the source (sun and sky), the calibration of the ultraviolet-intensity meter in absolute value may not be in great error. One object in making these erythemal tests was to correlate the biological response with the radiometric measurements, so that if a correction is required in the latter, a similar correction can be applied to the M. P. E. evaluations.

V. REFERENCES AND NOTES

[1] At the Oxford Meeting (Sept. 12 to 15, 1936) of the International Commission on Solar Radiation (Organization Meteorologique Internationale) the senior writer was appointed the U. S. A. representative on a subcommission to investigate the cadmium photoelectric cell for measuring ultraviolet solar radiation for use in medicine [6]. In this connection acknowledgement is made to the Council on Physical Therapy of the American Medical Association for two grants-in-aid to develop a photoelectric ultraviolet-intensity meter with a flat, horizontal receiving surface of Mg [3, 4], and to the American Philosophical Society for a subsequent grant-in-aid in the improvement of this type of ultraviolet-intensity meter, using Zr-photoelectric cells.

[2] W. W. Coblentz and R. Stair, Measurements of ultraviolet solar radiation in Washington, 1936 to 1942, J. Research NBS **30,** 435 (1943) RP1542.

[3] W. W. Coblentz and R. J. Cashman, *A photoelectric cell for measuring ultraviolet solar and sky radiation on a horizontal plane,* Bul. Am. Meteorol. Soc. **21,** 149 (1940).

[4] W. W. Coblentz, F. R. Gracely, and R. Stair, *Measurements of ultraviolet solar and sky radiation intensities in high latitudes,* J. Research NBS **28,** 581 (1942) RP1469.

[4a] Reference to the use of an automatic impulse ("traffic") counter and recorder is made in Tech. News Bul. NBS 289, p. 41 (May 1941). In figure 5 of J. Research NBS **31,** 181 (1943) RP1557 is given a photograph of the interior of such a traffic recorder as recently applied by L. F. Curtiss and F. J. Davis in a counting method for the determination of small amounts of radium and of radon.

[5] H. C. Rentschler, *An ultraviolet light meter,* Proc. Am. Inst. Elec. Engrs. **49,** 576 (1930); Trans. Illum, Engr. Soc. **25,** 406 (1930).

[6] W. W. Coblentz, *The spectral range of ultraviolet solar radiation useful in bioclimatology,* Bul. Am. Meteorol. Soc. **22,** 316 (1941).

[7] In conformity with recent terminology, in the present paper "phototube" is used as an abbreviation to designate the vacuum type of photoelectric cell, irrespective of the shape of the container, whether spherical or tubular in form.

[8] This type of construction was developed by H. C. Rentschler in connection with the pioneering measurements of ultraviolet radiation in American cities by James E. Ives and W. A. Gill (U. S. Public Health Service, Bulletin 233, March 1937); also the subsequent modifications by F. S. Brackett and his collaborators (Rev. Sci. Inst. **12,** 87, 1941), including the mounting of all the parts in an evacuated vitreous envelope, and the substitution of a flat surface [3] for the half-cylinder cathode previously used.

[9] W. W. Coblentz and R. Stair, *A portable ultraviolet-intensity meter, consisting of a balanced amplifier, photoelectric cell, and microammeter,* BS J. Research **12,** 23 (1934) RP647, [30].

[10] W. W. Coblentz and R. Stair, *Factors affecting ultraviolet solar-radiation intensities* J. Research NBS **15,** 123 (1935) RP816.

[11] W. W. Coblentz and R. Stair, *A standard source of ultraviolet radiation for calibrating photoelectric dosage intensity meters,* J. Research NBS **16,** 83 (1936)RP858.

[12] W. W. Coblentz, R. Stair, and J. M. Hogue, *A balanced thermocouple and filter method of ultraviolet radiometry, with practical applications,* BS J. Research **7,** 723 (1931) RP370.

A description is given of (a) the evaluation of ultraviolet solar radiation by means of a single thermocouple receiver [28] and a balanced (differential) thermopile receiver, (b) physiological tests of the erythematogenic efficiency of ultraviolet solar radiation, and (c) calibration of a photoelectrically operated impulse counter, in absolute units, by means of radiometric filter methods.

[13] W. W. Coblentz, R. Stair, and J. M. Hogue, *Tests of a balanced thermocouple and filter radiometer as a standard ultraviolet dosage intensity meter,* BS J. Research **8,** 759 (1932) RP450.

Data are given on the erythematogenic efficiency of ultraviolet radiation from various artificial sources and from the sun.

[14] W. W. Coblentz and R. Stair, *Evaluation of ultraviolet solar radiation of short wavelengths,* J. Research NBS **16,** 315 (1936) RP877.

Data are given showing a close agreement in the evaluation of ultraviolet solar radiation by means of (a) a balanced thermopile [12] calibrated in absolute units by means of a standard of thermal radiation [15], and (b) a Ti-photoelectric cell [9] calibrated in absolute value, against a standard of ultraviolet radiation [11].

[15] W. W. Coblentz and R. Stair, *The present status of the standards of thermal radiation maintained by the National Bureau of Standards,* BS J. Research **11,** 79 (1933) RP578.

[16] W. W. Coblentz and R. Stair, *Distribution of energy in the extreme ultraviolet of the solar spectrum,* J. Research NBS **17,** 1 (1936) RP899.

[17] W. W. Coblentz and R. Stair, *Radiometric measurements of ultraviolet solar intensities in the stratosphere,* Bul. Am. Meteorolog. Soc. **18,** 345 (1937); Radiologica **1,** 12 (1937).

[17a] R. Stair and W. W. Coblentz, *Radiometric measurements of ultraviolet solar intensities in the stratosphere,* J. Research NBS **20,** 185 (1938) RP1075.

The papers [17] give a brief description of the methods used and a preliminary report of the results obtained in the stratosphere flights of 1937. RP1075 gives the complete report of the results obtained.

[18] G. W. Bachman, School of Tropical Medicine, San Juan, Puerto Rico. Annual Report of the Director, 1936, 1938, 1939.

[19] G. W. Kenrick and H. Oritz, *Measurements of ultraviolet solar radiation in Puerto Rico,* Trans. Am. Geophys. Union (Meteorology Section) **38,** 134 (1938).

[20] G. W. Kenrick and G. DelToro Jr., *Studies in solar radiation and their relationship to biophysics and the general problem of climate and health,* Puerto Rico J. Pub. Health Trop. Med. **16,** 387 (1940).

[21] G. W. Kenrick, *An electronic integrator for counting circuit contacts, Electronics* **14,** 33 (1941).

A description is given of an integrating circuit that averages the impulses per minute [5] and traces the values continuously on a Leeds Northrup chart recorder. This gives a graphical indication of ultraviolet intensity and its variations with solar heights, clouds, etc. [20].

[22] M. Luckiesh, A. H. Taylor, and G. P. Kerr, *Ultraviolet energy in daylight—a two-year record,* J. Franklin Inst. **223,** 699 (1937); *A four-year record,* J. Franklin Inst. **228,** 425 (1939).

[23] F. Dannmeyer, *Die ultraviolette Himmelsstrahlung in nördlichen Breiten,* Strahlentherapie **35,** 607 (1930).

[24] Acknowledgement is made to Glenn A. Greathouse, Bureau of Plant Industry, for the use of several of his impulse-counting machines when not in use in the field.

[25] H. H. Kimball and H. E. Hobbs, *A new form of thermoelectric recording pyrheliometer,* J. Opt. Soc. Am. & Rev. Sci. Insts. **7,** 707 (1923); Monthly Weather Rev. **51,** 239 (1923).

[26] I. F. Hand, *Review of U. S. Weather Bureau solar radiation investigations,* Monthly Weather Rev. **65,** 415 (1937).

[27] W. W. Coblentz, *The hazard of burns from orificial ultraviolet applicators.* Arch. Phys. Therapy **23,** 149 (1942).

[28] W. W. Coblentz and R. Stair, *Measurement of extreme ultraviolet solar radiation by a filter method.* BS J. Research **6,** 951 (1931) RP318.

Measurements are given of the biologically effective component of ultraviolet solar radiation, at high altitudes and at sea level, using an exclusion filter and a single thermocouple receiver, calibrated in absolute value by simultaneous measurements of the total incident solar radiation with a standardized pyrheliometer [12]. See ref [14] for corrections to these early data.

[29] Our task was greatly simplified by an extensive table of solar heights on different dates, supplied by I. F. Hand of the U. S. Weather Bureau. If such

data are not obtainable from the local weather bureaus, the observer can use a theodolite.

[30] R. Stair and I. F. Hand, *A stable photoelectric amplifier and its application in ultraviolet and ozone studies*, Bul. Am. Meteorol. Soc. **22,** 259 (1941).

This paper describes a Wheatstone bridge type of balanced direct-current photoelectric amplifier [9] adapted for operation on 110-volt a-c commercial power lines. The output meter may be a portable or recording type of microammeter, galvanometer, or potentiometer. A mechanical device is proposed to perform an intregation of ultraviolet solar and sky radiation that is accomplished by the electronic intregrating device [5] used in the present investigation—see also [21].

[31] R. Stair and W. O. Smith, *A tungsten-in-quartz lamp and its applications in photoelectric radiometry*, J. Research NBS **30,** 449 (1943). RP 1543.

Description of a lamp consisting of a filament of tungsten wire inclosed in a spherical fused-quartz bulb proposed for use in irradiating large sized photoelectric receivers that are not readily calibrated for long-wave-length spectral response by means of filters, using a tungsten-ribbon-filament lamp [2, 32] having a fused-quartz window.

[32] R. Stair and W. W. Coblentz, Spectral Energy Distribution of the Standard Comparison Lamp Used in Evaluating the Flash Spectrum of the Solar Eclipse of 1940, Nat. Geographic Soc., Contrib. Tech. Papers, Solar Eclipse Series, No. 2, p. 48 (1942).

Description of spectral-energy measurements on the standard tungsten-ribbon lamp used in evaluating the photographic film densities of the flash spectrum in the range of wavelengths extending from 3450 to 5350 A; also a discussion of the spectral emissivities of tungsten by the junior author [34].

[33] R. Stair and I. F. Hand, *Methods and results of ozone measurements over Mount Evans, Colo.*, Monthly Weather Rev. **67,** 331 (1939).

A description is given of a "trial-and-error" method of calculating the amount of ozone in the stratosphere, based upon measurements with an ultraviolet intensity meter and filters (ref. [9] and fig. 1 in [10]). Unfortunately, cloudy weather prevented extensive (only 2) all-day measurements; but from the limited results obtained, the method appears promising.

[34] W. W. Coblentz, *The emissivity and energy distribution of tungsten in the photographic region of the spectrum*, Pub. Am. Astronom. Soc. **10,** 222 (1942).

Data are given on the spectral intensities of a standard tungsten-ribbon lamp, operated at 2,900°K, in the spectral range of wavelengths extending from 2500 to 11000 A, for use as a source of comparison in obtaining the spectral-energy distribution of celestial objects; also in determining by a filter method the long-wavelength spectral response of photoelectric cells used in ultraviolet-dosage-intensity meters [2].

[35] W. W. Coblentz, *Report to the Council on Physical Therapy on heliotherapy methods in some European sanatoriums*, J. Am. Med. Assn. **100,** 410 (1933).

At A. Rollier's sanatoriums in Leysin, Switzerland, in 1932, the writer saw a nontanning "Venetian blond" patient with surgical tuberculosis who was healed by sky radiation. Of course, the healing process was slower than by direct solar radiation, which could not be applied because of the weakness of the patient, whose nontanning skin could not tolerate direct solar radiation.

[36] A. R. Meetham, *The correlation of the amount of ozone with other characteristics of the atmosphere*, Quart. J. Roy. Meteorolog. Soc. (London) **63,** 289 (1937).

This paper gives an important discussion of phenomena in the stratosphere and their relation with observed sea level barometeric pressures. Dobson in the same volume, p. 305, points out that it is a matter of doubt whether the amount of ozone is affected by weather conditions or vice versa. See also an earlier paper by E. Kidson, Proc. Roy. Soc. (London) [A] **129,** 422 (1930). In recent times a better correlation is found between movements of tropical and polar air masses, and ozone concentration.

[37] In this connection, reference is made to a paper by M. Schein and B. Stoll, On *Rayleigh scattering of zenith skylight*, Helv. Physic. Acta **7,** 672 (1934), and to a discussion of the "reversal effect" (umkehreffekt) by F. W. P. Götz, *Die vertikale verteilung des atmosphärischen ozons*, Ergeb. Kosmischen Physik **III.** 253 (1938).

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SYNTHESIS OF VITAMIN C FROM PECTIC SUBSTANCES[1]

By Horace S. Isbell

ABSTRACT

A new process for the preparation of vitamin C from beet pulp and other pectic substances has been developed. The pectic substance is treated with a pectinase, the resulting galacturonic acid is separated in the form of a difficultly soluble salt which is reduced with hydrogen to a salt of L-galactonic acid. The salt is converted to L-galactono-lactone and oxidized to 2-keto-L-galactonic acid, which is lactonized and enolized to yield ascorbic acid (vitamin C). Electronic interpretations are presented for the conversion of methyl 2-keto-L-galactonate to ascorbic acid by basic catalysts, for the lactonization and enolization of 2-keto-hexonic acids by acid catalysts, and for the formation of furfural and reductic acid from pentoses, galacturonic acid, and ascorbic acid.

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I. INTRODUCTION

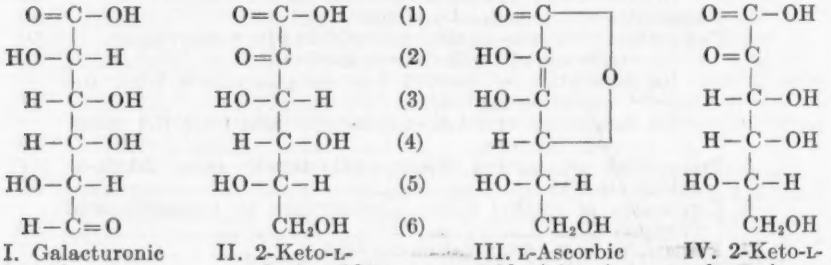
Because of the necessity of an adequate supply of vitamin C for the proper healing of wounds [1][2] an unprecedented demand for this sub-

[1] This paper was presented before the Division of Sugar Chemistry and Technology of the American Chemical Society at Cleveland, Ohio, April 5, 1944.

[2] Figures in brackets indicate the literature references at the end of this paper.

stance has been created by the present national emergency. Part of the requirements of the military and civilian populations is derived from fresh fruits and vegetables but this source is not adequate and must be supplemented by the synthetic vitamin. The process in present use for the synthesis of vitamin C [2] includes reduction of D-glucose to sorbitol, bacterial oxidation of this to L-sorbose, formation of diacetone sorbose, oxidation to diacetone-2-keto-L-gulonic acid, conversion to methyl 2-keto-L-gulonate followed by lactonization with the elimination of methanol, and rearrangement to ascorbic acid (vitamin C). As the process is long and complicated, it seemed desirable to seek a shorter method of synthesis.

To obtain the natural vitamin rather than an isomer thereof, it is necessary to use materials and reactions which lead to the L-*threo* configuration for carbons 4 and 5 of the product. Perhaps the most obvious raw material is galacturonic acid [3] and this was, in fact, used in the first synthesis of vitamin C [4]. The original method involved partial degradation and resynthesis of the molecule. It was not satisfactory for large scale production because it included the production of L-xylosone, a step which can be accomplished only with poor yield, and the preparation of galacturonic acid from D-galactose, a long and expensive process. Galacturonic acid, however, is an abundant natural carbohydrate, and methods have been developed in recent years for its preparation from plant materials. In the form of pectic substances, it comprises a large part of the pulp from citrus fruits and about 25 percent of the solids which remain after extraction of sugar from sugar beets. Since the annual production of sugar beets is approximately 7,000,000 tons, they provide a vast source of raw material which might be used for the production of galacturonic acid.



I. Galacturonic acid. II. 2-Keto-L-gulonic acid. III. L-Ascorbic acid (vitamin C). IV. 2-Keto-L-galactonic acid.

A comparison of the structures of galacturonic acid, I, 2-keto-L-gulonic acid, II, and L-ascorbic acid, III, reveals that galacturonic acid is isomeric with 2-keto-L-gulonic acid, a substance readily converted to ascorbic acid, and that the three compounds have the L-*threo* configuration for carbons 4 and 5. It was recognized early by Reichstein and Grüssner [5] that ascorbic acid usually occurs in plants containing large quantities of galacturonic acid, and attempts were made by them to rearrange galacturonic acid to ascorbic acid. The experiments gave highly reducing substances but did not yield appreciable quantities of ascorbic acid, and subsequently no method has been devised for effecting the conversion.

In the conversion of galacturonic acid to ascorbic acid, it is necessary to reduce the aldehyde group to $-CH_2OH$, and to oxidize either car-

bon 2 or carbon 3 so as to obtain an enediol without disturbing the configurations of carbons 4 and 5. Reduction of the aldehyde group is a simple matter and was part of the process originally used in the first synthesis [4]. The oxidation of either carbon 2 or carbon 3 is more difficult, but recently considerable progress has been made in the development of methods for the production of 2-keto-aldonic acids. Thus 2-keto-gluconic acid is now made by bacterial oxidation [6], and several methods have been devised for the oxidation of aldonic acids, in general, to 2-keto-aldonic acids [7]. Consideration of the probable mechanism for the enolization and lactonization of 2-keto-L-galactonic acid, discussed more fully on page 56, led to the premise that 2-keto-L-galactonic acid, IV, would yield ascorbic acid by an enolization and lactonization reaction, and that a new process for the production of ascorbic acid might include the following steps: Galacturonic

$$\text{acid} \xrightarrow{\text{hydrogenate}} \text{L-galactonic acid} \xrightarrow{\text{oxidize}} \text{2-keto-L-galactonic acid} \xrightarrow{\text{enolize and lactonize}} \text{ascorbic acid (vitamin C).}$$

At the time the investigation was begun it was known that esters of 2-keto-aldonic acids by treatment with sodium methylate undergo enolization and lactonization reactions with the formation of ascorbic acids [8]. However, it was generally believed that an ester of 2-keto-L-gulonic acid was necessary to obtain vitamin C (see p. 171 of [9]). 2-Keto-L-galactonic acid differs from 2-keto-L-gulonic acid only in the configuration of carbon 3, and consequently it was of academic as well as of practical interest to attempt the synthesis by the method outlined above.

Inasmuch as a successful process would require a cheap source of galacturonic acid or its salts, attention was directed first to the study of the salts of galacturonic acid with the object of obtaining one which could be used for separating galacturonic acid from the hydrolytic liquor of beet pulp. The investigation, which was conducted with Harriet L. Frush [10], led to the preparation of 12 new salts of galacturonic acid, including at least 4 which can be used for separating galacturonic acid from the hydrolytic liquor. The double salts of sodium and calcium, and of sodium and strontium, appear to be most satisfactory. By neutralization of the hydrolyzate from beet pulp with sodium carbonate and calcium carbonate in suitable proportion, followed by concentration of the solution, crystalline sodium calcium galacturonate was obtained in yield corresponding to about 18 percent of the dry pulp, or approximately 70 percent of the galacturonic acid content of the hydrolyzate.

Prior to the present investigation it was known that salts of galacturonic acid on reduction with either sodium amalgam [4, 11] or with hydrogen in the presence of catalysts [12] give salts of L-galactonic acid. Reduction of calcium galacturonate, sodium calcium galacturonate, or sodium strontium galacturonate, with hydrogen, in the presence of Raney nickel, gave salts of L-galactonic acid in nearly quantitative yield. Treatment of the salts with a chemically equivalent quantity of sulfuric acid, and dehydration, gave L-galactono-γ-lactone in good yield. Several of the methods reported in the literature [7] for the oxidation of aldonic acids to the corresponding 2-keto-acids were investigated and the oxidation of galactono-γ-lactone with

sodium chlorate in the presence of vanadium oxide [7c] was found to be the most satisfactory. Improvements were made in the procedure for isolating the product, and 2-keto-L-galactonic acid and 2-keto-D-galactonic acid were obtained in the crystalline state. The acids were converted to the crystalline methyl esters and these substances were lactonized and rearranged by the sodium methylate method [8]. The product from methyl 2-keto-L-galactonate on acidification gave a crystalline acid which proved to be L-ascorbic acid (vitamin C); by similar treatment methyl 2-keto-D-galactonate gave the crystalline enantiomorph, D-ascorbic acid. Thus the entire process was carried through as originally planned.[3]

It will be observed from the accompanying diagram that the process is relatively simple. Theoretically, 0.7 part by weight of ascorbic acid might be derived from 1 part by weight of sodium calcium galacturonate. The yield of ascorbic acid from sodium calcium galacturonate in the present study was approximately 20 percent of the theoretical, or 14 percent by weight, and the yield of sodium calcium galacturonate from beet pulp was 18 percent by weight. Thus 1 ton (2,000 lb) of dry beet pulp would yield approximately 50 pounds of ascorbic acid. The low yield is due in large measure to the lack of a highly efficient method for oxidizing L-galactonic acid to 2-keto-L-galactonic acid. Undoubtedly this step, as well as other steps in the process, will be improved so that ultimately the new process will compare favorably with the sorbose process.[4]

NEW PROCESS FOR THE PREPARATION OF ASCORBIC ACID.

Beet pulp —(hydrolysis)→ sodium calcium galacturonate (15 to 20% of weight of dry pulp) —(hydrogenation)→

sodium L-galactonate and calcium L-galactonate (over 90% yield) →

L-galactono-γ-lactone (over 90% yield) —(oxidation)→ 2-keto-L-galactonic acid (25 to 30% yield) —(esterification)→

methyl 2-keto-L-galactonate (over 90% yield) —(lactonization and enolization)→ ascorbic acid (over 90% yield)

II. EXPERIMENTAL PROCEDURE

1. PREPARATION OF SODIUM CALCIUM GALACTURONATE[5]

(a) FROM BEET PULP

A solution of galacturonic acid was prepared by enzymic hydrolysis of beet pulp in much the same manner as in the preparation of galac-

[3] In July 1942, the author filed patent applications relating to several phases of the problem, including the preparation of sodium calcium galacturonate from beet pulp. However, the same process was the subject of an application filed seven months earlier by Pasternack and Regna. The latter matured into United States Patent 2,338,534, January 4, 1944. A recent publication by Regna and Caldwell [13] reports the preparation of crystalline 2-keto-D-galactonic acid, and its successive conversion to methyl 2-keto-D-galactonate and to D-ascorbic acid. It is therefore apparent that others have been engaged also in a study of the synthesis of vitamin C from pectic substances and have developed independently, essentially the same process as that worked out by the present author.

[4] Possibly an organism will be found for oxidizing L-galactonic acid, in manner analogous to the oxidation of D-gluconic acid to 2-keto-D-gluconic acid.

[5] See footnote 3.

turonic acid from pectic acid [14]. In a typical preparation, 1 kg of dried beet pulp was suspended in 10 liters of water and mixed with 100 g of Pectinol 100 D.[6] The material was kept at 40° C and protected from mold growth by a layer of toluene. After 7 days the mixture was filtered. The residue was washed with hot water and finally discarded. The hydrolyzate (pH 3.4) was neutralized with a mixture of sodium carbonate and calcium carbonate in the proportion of one atom of sodium to one of calcium, and was concentrated in a vacuum still to a convenient volume. The crystals that formed were separated, washed with water, and dried. The yield of sodium calcium galacturonate hexahydrate thus obtained was 180 g. It was recrystallized from hot water and used for the preparation of calcium L-galactonate.

(b) FROM PEELS OF CITRUS FRUIT

Application of the process described in the foregoing paragraph to citrus fruit peels in place of beet pulp gave 55 g of sodium calcium galacturonate from 1 kg of moist orange peel, and 60 g of sodium calcium galacturonate from 1 kg of moist grapefruit peel. The amounts of water and Pectinol used in these experiments were half of those used with dry beet pulp.

2. PREPARATION OF CALCIUM L-GALACTONATE

The reduction of salts of galacturonic acid to salts of L-galactonic acid by the action of sodium amalgam was a step in the original synthesis of vitamin C [4]. Subsequently, reduction with hydrogen and a nickel catalyst has been used by Tipson [15] and others for the preparation of derivatives of L-galactonic acid, and a German patent [12] discloses the catalytic reduction of salts of galacturonic acid. The procedure employed in the present investigation is an adaptation of a method [16] reported to give high yields of sorbitol from glucose.

(a) FROM CALCIUM GALACTURONATE

Seventy grams of calcium galacturonate [10], 400 ml of water, and a nickel catalyst were placed in a bomb and treated with hydrogen at a pressure of 1,000 lb. and a temperature of 80° to 100° C. The catalyst was prepared from 20 g of Raney nickel alloy by digesting it with 200 ml of 25-percent aqueous sodium hydroxide for a period of 2 hours, and washing it with water. After 6 hours of hydrogenation, a negative test for copper-reducing substances indicated complete reduction of the calcium galacturonate. The bomb was emptied and rinsed with hot water, and the solution containing the reduction product was filtered. Evaporation of the filtered solution resulted in the crystallization of calcium L-galactonate. The crystalline salt was collected on a filter, washed with water, and dried at room temperature. The yield was 72 g, corresponding to 85 percent of the theoretical.

(b) FROM SODIUM CALCIUM GALACTURONATE

One hundred fifty grams of sodium calcium galacturonate, 500 ml of water, and a nickel catalyst were placed in a bomb and treated with hydrogen, at a pressure of 1,500 lb and a temperature of 80° C.

[6] A commercial pectinase manufactured by Rohm & Haas, Philadelphia, Pa. See Willaman and Kertesz, United States Patent 1,932,833, Oct. 31, 1933.

The catalyst was prepared from 20 g of Raney nickel alloy. After 6 hours of hydrogenation the solution containing the reduction product was filtered and, after the addition of 25 g of calcium nitrate, concentrated in a vacuum still to about 100 ml. The crystals of calcium L-galactonate which formed were separated, washed with cold water, dried, and weighed. The yield (140 g) was 93 percent of the theoretical.

The hydrogenations described above were conducted at high pressures because suitable equipment was available and convenient. Hydrogenations under conditions similar to those given, but at pressures of 15 to 30 lb, gave equally satisfactory yields of calcium L-galactonate but required more time.

3. PREPARATION OF L-GALACTONO-γ-LACTONE

A dry mixture containing 1 mole of calcium L-galactonate and 1 mole of oxalic acid was added with stirring to 1 liter of hot water. The resulting calcium oxalate was separated by filtration, and the filtrate was evaporated to dryness at 80° C under reduced pressure. The L-galactono-γ-lactone, which crystallized in nearly quantitative yield, was recrystallized from ethyl alcohol. The optical rotation and melting point of the product ($[\alpha]_D^{20}=+78°$ and mp 134° C) are in agreement with the constants reported for L-galactono-γ-lactone by Richtmyer, Hann, and Hudson [17].

4. PREPARATION OF 2-KETO-L-GALACTONIC ACID AND ITS METHYL ESTER

(a) OXIDATION OF L-GALACTONO-γ-LACTONE

One hundred eighty grams of L-galactono-γ-lactone, 1 liter of anhydrous methyl alcohol, 30 g of sodium chlorate, 2 g of vanadium pentoxide, and 3.5 g of phosphoric anhydride were placed in a 2-liter glass-stoppered flask and shaken mechanically for several days. When all of the chlorate had reacted, as shown by a change in color from brown to greenish blue, the solution was filtered and the solid material, largely vanadium pentoxide, was discarded. The procedure followed to this point differs from that described by Pasternack and Regna [7c] only in that phosphoric anhydride was used in place of phosphoric acid. The phosphoric anhydride causes rapid esterification of the lactone, with the result that the galactono-lactone is converted to methyl galactonate prior to oxidation. An analysis of the solution containing the oxidation product revealed the presence of copper-reducing substance corresponding to 54 g of 2-keto-L-galactonic acid. The filtered solution was mixed with 10 g of cadmium carbonate and concentrated under reduced pressure in a vacuum still. As the evaporation proceeded, crystals separated from solution. When the material in the distillation flask reached a pasty consistency it was diluted with 200 ml of isopropyl alcohol and seeded with crystalline methyl L-galactonate.

After 18 hours at 0° C, the solid material was separated from the alcoholic solution by filtration. The solids (110 g) consisted of methyl L-galactonate, L-galactono-γ-lactone and sodium chloride. The alcoholic solution contained methyl 2-keto-L-galactonate with small quantities of L-galactono-γ-lactone, methyl L-galactonate, methyl oxalate, and other esters not yet identified. In a manufacturing process the

residue could be used in place of fresh L-galactono-γ-lactone. In the present case, however, the methyl L-galactonate and the gamma lactone in the solid residue were reclaimed in the form of cadmium L-galactonate. The salt reclaimed corresponded to 60 g of L-galactono-γ-lactone. Inasmuch as the solution contained 54 g of 2-keto-L-galactonic acid, by analysis, the yield of 2-keto-L-galactonic acid in solution was 41 percent of the theoretical amount based on the weight of lactone used and not recovered. The alcoholic solution containing the oxidation product was used for the preparation of methyl 2-keto-L-galactonate, and a similar solution obtained in a duplicate experiment was used for the preparation of 2-keto-L-galactonic acid.

(b) SEPARATION OF METHYL 2-KETO-L-GALACTONATE FROM THE OXIDATION MIXTURE

The isopropyl alcoholic solution obtained by the oxidation of 180 g of L-galactono-γ-lactone described in the preceding section was evaporated under reduced pressure to a thick sirup. This sirup was triturated with ten 100-ml portions of warm acetone, and the residue was discarded. The acetone extracts were combined and concentrated in a vacuum still to remove the acetone. The residual sirup (50 g) was dissolved in 50 ml of isopropyl alcohol, seeded with methyl 2-keto-L-galactonate and placed in a refrigerator. After 18 hours the resulting crystals were separated by filtration, washed with isopropyl alcohol, and dried. A microscopic examination of the crystals showed two substances: One, L-galactono-γ-lactone, was present in chunky truncated crystals; the other, methyl 2-keto-L-galactonate was present in long slender crystals, usually pointed at both ends. The crystalline mixture weighed 25 g and the copper-reducing value indicated that the material contained about 80 percent of methyl 2-keto-L-galactonate. The mixture melted at 125° to 130° C $[\alpha]_D^{20}=+20°$. The mother liquor gave a second crop of crystals (2 g), which melted at 140° C $[\alpha]_D^{20}=+6°$. The material was nearly pure methyl 2-keto-L-galactonate. The lactone-ester mixture obtained in the first crop was fractionally recrystallized from isopropyl alcohol. By alternately seeding with the gamma lactone, removing a crop of crystals rich in the lactone, and then seeding the residual mother liquor with the ester, several small fractions of L-galactono-γ-lactone were obtained and about 5 g of methyl 2-keto-L-galactonate, which melted at 145° to 148° C. $[\alpha]_D^{20}=+4.7°$.

Separation of methyl 2-keto-L-galactonate from the solution obtained by oxidation of L-galactono-γ-lactone provides material which can be converted directly to ascorbic acid. But since the separation of the ester from the accompanying impurities is difficult, and 2-keto-L-galactonic acid is easily purified, it seems more practicable at present to hydrolyze the crude ester, separate the resulting 2-keto-L-galactonic acid in the pure crystalline state, and reconvert it to the methyl ester as described in the next section.

(c) SEPARATION OF 2-KETO-L-GALACTONIC ACID FROM THE OXIDATION MIXTURE

An isopropyl alcoholic solution obtained by the oxidation of 180 g of L-galactono-γ-lactone, as described on page 50, was evaporated under reduced pressure to a sirup, which was dissolved in 2 liters of water containing 2 ml of acetic acid. The solution was heated to boiling in a flask connected with a reflux condenser. From time to

time small samples were taken, and the acidity was determined by titration with standard alkali (bromthymol blue indicator). The titration showed that hydrolysis was complete in 4 hours, at which time the solution was transferred to a vacuum still and concentrated to a thick sirup. During the evaporation, crystals of 2-keto-L-galactonic acid formed. The mixture of sirup and crystals was diluted with an equal volume of acetic acid and placed in a refrigerator for crystallization to take place. After 1 day the crystals were collected on a filter, washed with aqueous acetic acid, and dried. The first crop of crystals (mp 168° C) weighed 30 g. Additional crops obtained from the mother liquor were mixtures of 2-keto-L-galactonic acid and L-galactono-γ-lactone, from which 2 g of pure 2-keto-L-galactonic acid was obtained. Since the first crop was substantially pure 2-keto-L-galactonic acid, the yield of the crystalline acid was 32 g. This is approximately 60 percent of the amount shown by analysis or 24 percent of the theoretical, based on the amount of L-galactono-γ-lactone used and not reclaimed.

The material used for analysis and for the determination of optical rotation and other properties was recrystallized by dissolving the crude acid in 2 parts of hot water, filtering the solution with the aid of a little decolorizing carbon, and evaporating it under reduced pressure in the presence of seed crystals. The crystals of pure 2-keto-L-galactonic acid which formed were collected on a filter, washed with cold water, and dried, at room temperature, over calcium chloride: mp 170° C; $[\alpha]_D^{20}=+5.2°$ (water, c=4). Analysis: Calculated for $C_6H_{10}O_7$: C, 37.1; H, 5.2. Found: C, 37.2; H, 5.5.

2-Keto-L-galactonic acid separates from impure sirups in truncated plates, which, if undisturbed, form in rosette-like clusters. On recrystallization, the crystals become thicker and more prismatic.

5. PREPARATION OF METHYL 2-KETO-L-GALACTONATE FROM 2-KETO-L-GALACTONIC ACID

The esterification of 2-keto-L-galactonic acid can be carried out by the methods developed for the esterification of 2-keto-gulonic acid [18].

Ten grams of 2-keto-L-galactonic acid was refluxed with 100 ml of anhydrous methyl alcohol containing 1.5 g of hydrogen chloride. After 2 hours the solution was cooled and the hydrogen chloride was neutralized by the addition of silver carbonate. The resulting silver chloride was separated by filtration; the filtrate was evaporated under reduced pressure at 35° C to a volume of 12 ml. The concentrated sirup was diluted with 20 ml of acetone, and petroleum ether was added to the point of saturation. The mixture was allowed to stand overnight in the refrigerator. The crystals of methyl 2-keto-L-galactonate which formed were collected on a filter and washed with a mixture of acetone and ligroin in the proportions of 1:2. The air-dried crystals obtained in the first crop weighed 5 g, and in addition, 2 g was separated from the mother liquor. Although the yield was only 70 percent, a higher yield could be obtained by cycling the mother liquor. In a large-scale operation, an azeotropic distillation and dehydration process could be employed in place of the procedure described here.

Seven and one-half grams of the ester was recrystallized by dissolving it in 50 ml of hot anhydrous methyl alcohol, filtering the solution, cooling it to room temperature, and adding about 75 ml of a mixture consisting of 2 parts by volume of acetone and 1 part of ligroin. The crystals which formed in the course of several hours were separated by filtration, washed with a mixture of acetone and ligroin, and dried over calcium chloride and paraffin at room temperature $[\alpha]_D^{20}=+4.7°$ (water, c=4). Analysis: Calculated for $C_7H_{12}O_7$:C, 40.4; H, 5.8. Found: C, 40.2; H, 5.9.

The substance has an agreeable sweet taste. It reduces alkaline copper reagents even at room temperature. The melting point varies widely, according to the method of measurement. In Pyrex tubes the compound melts at 145° to 150° C, depending upon the rate of heating, but in soft-glass tubes the melting point is depressed at least 10 degrees, presumably through the effect of the alkali in the glass in causing rearrangement. The presence of an unaltered 2-keto-L-galactonate structure in the ester was established by regeneration of 2-keto-L-galactonic acid in the following manner: A 0.5-g sample of the ester was dissolved in 10 ml of water containing 1 drop of concentrated hydrochloric acid. The solution was placed in a beaker and allowed to evaporate at room temperature. After 24 hours a crystalline residue remained, which melted at 168° to 170° C, and did not lower the melting point of an authentic sample of 2-keto-L-galactonic acid.

6. CONVERSION OF METHYL 2-KETO-L-GALACTONATE TO L-ASCORBIC ACID (VITAMIN C)

Two grams of crystalline methyl 2-keto-L-galactonate was added at room temperature, and in the absence of oxygen to 15 ml of 0.7 *N* sodium methylate in absolute alcohol. In a few minutes the methyl 2-keto-L-galactonate went into solution and shortly thereafter a light-yellow sodium salt precipitated. After 15 minutes a quantity of 1 *N* sulfuric acid (in 75-percent aqueous isopropyl alcohol), equivalent to the sodium methylate previously used, was added from a burette. The solution was diluted with 10 ml of isopropyl alcohol, and the resulting crystalline sodium sulfate was separated by filtration. The filtrate was concentrated in a vacuum to a sirup, which crystallized. The crystals were collected on a filter, washed with tertiary amyl alcohol, and dried in a vacuum at room temperature. $[\alpha]_D^{20}=23°$ (water, c=4). The product (1.2 g) melted at 190° to 192° C, and a mixed melting-point determination with authentic L-ascorbic acid showed no depression. Hence the material is L-ascorbic acid. Analysis: Calculated for $C_6H_8O_6$:C, 40.9; H, 4.6. Found: C, 40.9; H, 4.6.

7. PREPARATION OF 2-KETO-D-GALACTONIC ACID

The preparation of 2-keto-D-galactonic acid from D-galactosone was reported in 1929, [19], but the crystalline acid was not prepared until recently [13]. The crystalline acid was obtained also in the course of the present investigation. D-galactono-γ-lactone was oxidized and 2-keto-D-galactonic acid was isolated in the manner described in sections 4(a) and 4(c) for the enantiomorphs. The yield of 2-keto-D-galactonic acid from 180-g samples of D-galactono-γ-

lactone varied from 25 to 35 g. The acid was recrystallized from hot water and was dried at room temperature over calcium chloride in a vacuum desiccator. Melting point 170° C. $[\alpha]_D^{20}=-5.2°$ (water, c=5). Analysis: Calculated for $C_6H_{10}O_7$:C, 37.1; H, 5.2. Found: C, 37.1; H, 5.5.

Regna and Caldwell [13] report a melting point of 170° to 171° C and $[\alpha]_D^{20}=-6.7°$ (water, c=1.2).

The acid reduces alkaline copper reagents. The reducing power of the acid by the modified Scales method [20] is about 93 percent of the reducing power of glucose.

8. PREPARATION OF METHYL 2-KETO-D-GALACTONATE

Crystalline methyl 2-keto-D-galactonate was prepared from the oxidation product of D-galactono-γ-lactone in the manner given on page 51 for the preparation of the enantiomorphic substance, methyl 2-keto-L-galactonate. The substance was prepared also by esterification of 2-keto-D-galactonic acid by the method described on page 52. Analysis: Calculated for $C_7H_{12}O_7$:C, 40.4; H, 5.8. Found: C, 40.4; H, 5.9. The melting point, like that of the L isomer, varies widely, according to the method of measurement. In Pyrex tubes, rapidly heated, the compound melts at 145° to 150°C; in soft-glass tubes, purchased from a chemical supply company, it melted at about 135° C. $[\alpha]_D^{20}=-4.6°$ (water, c=1.7).

For methyl 2-keto-D-galactonate, Regna and Caldwell [13] have reported: mp 138° to 139° C; $[\alpha]_D^{20}=-11.3°$ (water, c=1.2). The melting point lies within the range observed in the present study, but the optical rotation differs widely.

The substance has a sweet taste. It is sensitive to alkaline oxidation agents and reduces Fehling's solution slowly at room temperature.

9. CONVERSION OF METHYL 2-KETO-D-GALACTONATE TO D-ASCORBIC ACID

Two grams of crystalline methyl 2-keto-D-galactonate was treated with sodium methylate and the product was worked up in the manner described for the preparation of L-ascorbic acid from methyl 2-keto-L-galactonate. The crude product weighed 1.1 g and had a specific rotation of −25°. After recrystallization from aqueous acetic acid, the substance had a melting point of 191° C. $[\alpha]_D^{20}=-23.8$ (water, c=3), in agreement with the specific rotation of D-ascorbic acid. Analysis: Calculated for $C_6H_8O_6$: C,40.9; H,4.6. Found: C,40.9; H,4.7.

The production of D-ascorbic acid from methyl 2-keto-D-galactonate corroborates the work of Regna and Caldwell [13].

III. ELECTRONIC INTERPRETATIONS

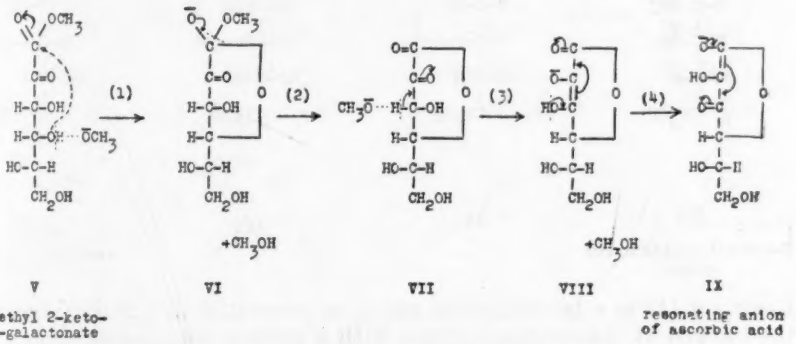
The principle of consecutive electron displacement (previously used by the author to account for numerous reactions in the carbohydrate field [21]) furnishes a satisfactory basis for the interpretation of many reactions related to the synthesis of ascorbic acid. The fundamental concept is, that the peculiar properties of systems involving double bonds may be explained by the migration of electrons from points of high electron density to points of lower electron density, frequently

with the addition and elimination of ions.[7] Nearly all of the reactions are induced by the formation of intermediate complexes with acid catalysts or with basic catalysts. In the equations that follow, dotted lines connecting two groups indicate the formation of intermediate complexes; dotted lines separating groups represent points of cleavage, and curved arrows indicate the displacement of electrons under the influence of the attacking agent. In reactions catalyzed by acids, the proton donor is represented somewhat arbitrarily as H^+.

1. LACTONIZATION AND ENOLIZATION OF METHYL 2-KETO-L-GALACTONATE BY SODIUM METHYLATE

The rearrangement of methyl 2-keto-L-galactonate to the anion of L-ascorbic acid is represented by formulas V to IX. Reaction (1) is promoted by combination of the hydrogen of the hydroxyl on carbon 4 with the methylate ion. This is followed by cleavage of methyl alcohol and the formation of an intermediate VI having an ortho acid structure. This hypothetical substance is similar to intermediates which have been postulated in the hydrolysis of esters (see p. 395 of

FORMATION OF ASCORBIC ACID FROM METHYL 2-KETO-L-GALACTONATE



V: methyl 2-keto-L-galactonate

IX: resonating anion of ascorbic acid

[23]). Decomposition of the intermediate yields a ketonic lactone VII which gives ascorbic acid by enolization. Each mole of the ester V converted to sodium ascorbate requires 1 mole of sodium methylate. The methylate anion is converted to methyl alcohol, and the sodium ion combines with the anion of ascorbic acid. The formulas arbitrarily represent the lactonization reaction as preceding the enolization reaction. The changes may take place simultaneously, or even in the reverse order; in any case, substantially the same interpretation applies.

At first glance the arrangement of the groups about the double bond of ascorbic acid might be expected to give rise to a *cis* and a *trans* isomer. However, the *trans* isomer is not possible, because a *trans* arrangement of the hydroxyl groups about the double bond places carbons 1 and 4, also, in the *trans* position, and prevents ring closure. In some respects the ring of ascorbic acid is comparable to that of maleic anhydride, whereas a *trans* isomer would be comparable to an anhydride of fumaric acid, a structure incapable of existence. During the conversion of the methyl 2-keto-ester to ascorbic acid, the asymmetry of carbon 3 is

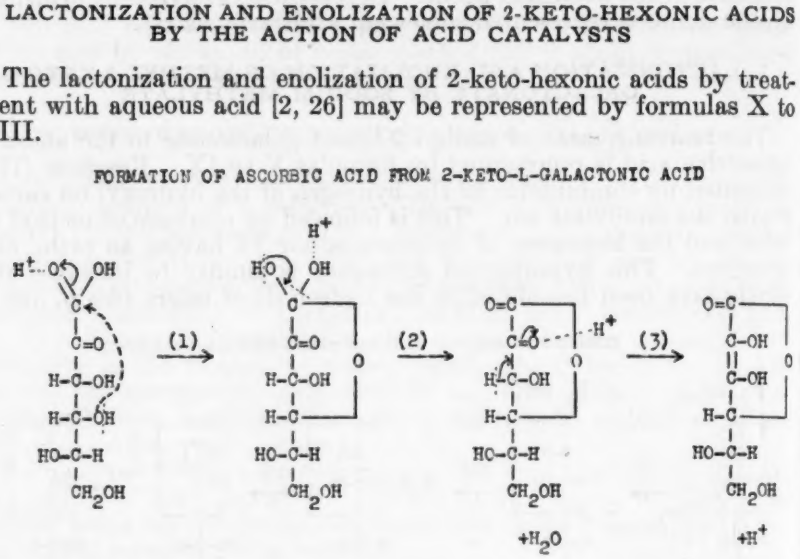
[7] General discussions of this concept may be found in [22, 23, 24, 25].

destroyed through the enolization reaction and the subsequent formation of a resonating structure. Hence substances which differ merely in the configuration of carbon 3 would be expected to yield the same product. The configurations of carbons 4 and 5, however, are retained, and the different configurations for these carbons give rise to four isomers, namely D- and L-ascorbic acid, and D- and L-isoascorbic acid.

2. LACTONIZATION AND ENOLIZATION OF 2-KETO-HEXONIC ACIDS BY THE ACTION OF ACID CATALYSTS

The lactonization and enolization of 2-keto-hexonic acids by treatment with aqueous acid [2, 26] may be represented by formulas X to XIII.

FORMATION OF ASCORBIC ACID FROM 2-KETO-L-GALACTONIC ACID



X
2-keto-L-galactonic acid

XI

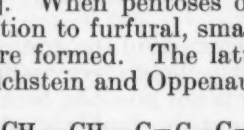
XII

XIII
ascorbic acid

Reaction (1) is a lactonization reaction promoted by combination of the oxygen of the carboxyl group with a proton, and the approach of the oxygen of carbon 4 to carbon 1; reaction (2) depicts a mechanism for the decomposition of the ortho acid intermediate. The electronic changes indicated in formula XI account for the instability of two hydroxyls attached to a single carbon.

3. FORMATION OF FURFURAL AND REDUCTIC ACID FROM PENTOSES, GALACTURONIC ACID, AND ASCORBIC ACID

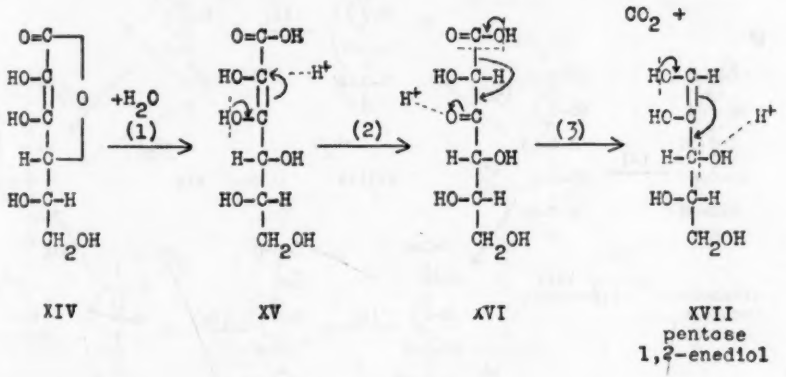
When ascorbic acid is heated with 12-percent hydrochloric acid, furfural is evolved [27]. When pentoses or hexuronic acids are similarly treated, in addition to furfural, small quantities of a strongly reducing, enolic acid are formed. The latter substance was named "reductinsäure" by Reichstein and Oppenauer [28] and was shown to be

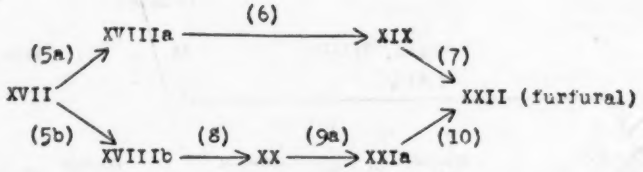


The name was translated in English to "reductic acid." The reactions for the formation of reductic acid and furfural appear to be related, and explicable by means of consecutive electron displacements.

The production of furfural from ascorbic acid is represented by the reactions of formulas XIV to XVII followed by the reactions given for the pentoses in formulas XVII to XXII. According to the hypothetical reactions, furfural is derived from both ascorbic acid and the pentoses through the intermediate production of a pentose 1, 2-enediol, XVII. In the case of the pentoses, the 1, 2-enediol yields reductic acid, presumably by reactions (5b), (8), (9b), (11), (12), (13), and (14). Inasmuch as the 1, 2-enediol appears to be formed from ascorbic acid, as well as from the pentoses, one might expect that a closer study of the reaction of ascorbic acid with aqueous acid would also reveal the formation of small amounts of reductic acid. The 1, 2-enediol of L-xylose is obtained from the beta ketonic acid, XVI, through the cleavage of carbon dioxide, reaction (3). The diagram accounts

FORMATION OF FURFURAL FROM ASCORBIC ACID

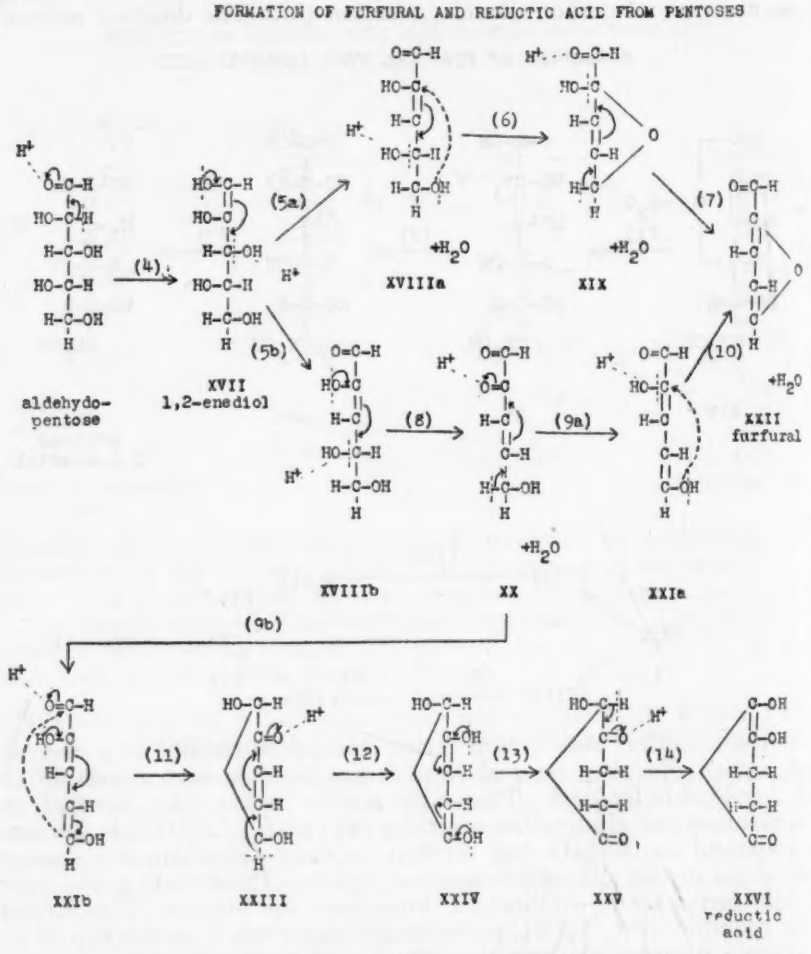




for the fact that beta ketonic acids decompose readily with cleavage of carbon dioxide. Several courses are possible for converting the 1, 2-enediol to furfural. They differ mainly in the order in which the cyclization and elimination reactions take place. XVIIIb is the same compound as XVIIIa but written to show the electronic changes involved in the alternative reaction course. Possibly ring and open-chain forms are in equilibrium throughout the process. The formula for reductic acid, XXVI, is written with carbon 2 at the top of the formula in order to show the relationship to the preceding intermediates. The substance contains an enediol group adjacent to a carbonyl group. Presumably, its anion has a resonating structure analogous to that of the anion of ascorbic acid, IX. The substance of formula XXI was previously suggested by Aso as a possible intermediate in the formation of reductic acid [29]. The mechanism for the forma-

tion of furfural is similar to that suggested by the present author for the formation of furfural from methyl pentoses [21]

The formation of furfural and reductic acid from galacturonic acid by treatment with aqueous acid is explained by the reactions of formulas XXVII to XXXIII. The elimination of carbon dioxide, reaction (18), is similar to the elimination of carbon dioxide from beta ketonic acids, mentioned in connection with formula XVI. According to the suggested mechanism, carbon dioxide is liberated, not from galacturonic acid with the formation of L-arabinose, as frequently assumed, but from an unsaturated intermediate obtained by enolization and de-enolization reactions. Reactions (16a), (17), and (18)

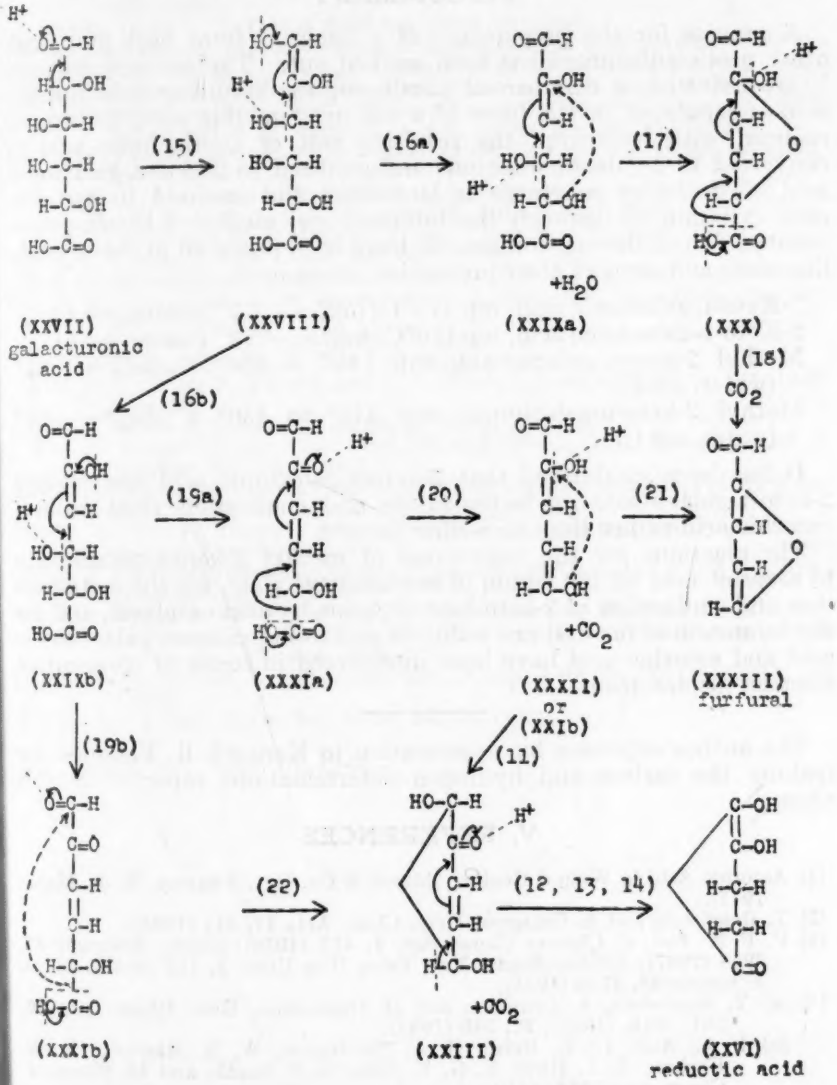


represent the cyclization reaction as preceding the elimination of carbon dioxide, whereas reactions (16b), (19a), (20), and (21) show an alternative course in which the cyclization reaction is last.

In the formation of reductic acid from galacturonic acid, two courses are shown for the conversion of XXXI to XXIII, a substance

which yields reductic acid by enolization and ketonization reactions. In one mechanism, the elimination of CO_2 and cyclization are represented as successive steps, reactions (20) and (11); in the other mechanism, elimination of CO_2 and cyclization occur in one step, reaction (22).

FORMATION OF FURFURAL AND REDUCTIC ACID FROM GALACTURONIC ACID



The possibility of two reaction mechanisms for the formation of reductic acid from galacturonic acid and only one for its formation from the pentoses may account for the higher yield of this substance from galacturonic acid. Supposedly, in both cases, the formation of reductic acid is promoted by combination of the acid catalyst with the

carbonyl group of carbon 1. This leaves a low electron density at carbon 1, a condition which is rectified by a shift of electrons from carbon 5, obtained in the case of XXIb by ketonization of the enolic group at carbon 2 and in the case of XXXIb by elimination of the carboxyl group as carbon dioxide.

IV. SUMMARY

A process for the preparation of vitamin C from beet pulp and other pectic substances has been worked out. The pectic substance is treated with a commercial pectinase; the resulting galacturonic acid is separated in the form of a difficulty soluble salt; the salt is reduced with hydrogen; the resulting salt of L-galactonic acid is converted to L-galactono-lactone and oxidized to 2-keto-L-galactonic acid. The latter substance is lactonized and enolized to ascorbic acid (vitamin C) through the intermediate, methyl 2-keto-L-galactonate. The following compounds have been prepared in the crystalline state and some of their properties determined:

2-Keto-L-galactonic acid, mp 170°C; $[\alpha]_D^{20}=+5.2°$ (water, c=4).
2-Keto-D-galactonic acid, mp 170°C; $[\alpha]_D^{20}=-5.2°$ (water, c=5).
Methyl 2-keto-L-galactonate, mp 145° to 150° C; $[\alpha]_D^{20}=+4.7°$ (water, c=4).
Methyl 2-keto-D-galactonate, mp 145° to 150° C; $[\alpha]_D^{20}=-4.6°$ (water, c=1.7).

It has been established that 2-keto-L-galactonic acid and methyl 2-keto-L-galactonate on lactonization and enolization yield natural ascorbic acid rather than an isomer thereof.

The reactions for the conversion of methyl 2-keto-L-galactonate to ascorbic acid by the action of sodium methylate, for the lactonization and enolization of 2-keto-hexonic acids by acid catalysts, and for the formation of furfural and reductic acid from pentoses, galacturonic acid and ascorbic acid have been interpreted in terms of consecutive electron displacement.

The author expresses his appreciation to Kenneth R. Fleischer for making the carbon and hydrogen determinations reported in this paper.

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SPECIFIC HEAT AND INCREASES OF ENTROPY AND ENTHALPY OF THE SYNTHETIC RUBBER GR-S FROM 0° TO 330° K

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ABSTRACT

Specific heat measurements were made over the range 12° to 330° K on a sample of synthetic rubber GR–S (Buna S) by means of an adiabatic vacuum-type calorimeter. A Debye specific heat function was used to calculate values below 15° K. At about −61° C the material undergoes a transition of the second order, the specific heat increasing rapidly by about 40 percent. From −50° to +60° C, the specific heat values can be calculated to within 0.1 percent by the equation $C_p = 0.4346 + 7.029 \times 10^{-4}\ t + 1.156 \times 10^{-6}\ t^2$ in calories gram^{-1} degree Kelvin^{-1}. At 25° C the specific heat is 1.894 international joules gram^{-1} degree Kelvin^{-1} (0.4528 calorie gram^{-1} degree Kelvin^{-1}). The increase in entropy from 0° to 298.16° K is calculated to be 1.824 international joules gram^{-1} degree Kelvin^{-1} (0.4359 calorie gram^{-1} degree Kelvin^{-1}). Values of specific heat, and increases of entropy, enthalpy, and free energy are tabulated at 5-degree intervals. The experimental data indicate that values below the transition are dependent upon the thermal history of the sample. This phenomenon, as well as the temperature drifts observed, can be explained on the theory that the transition results from an increasingly slow approach to the equilibrium state at temperatures in the transition region and below.

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I. INTRODUCTION

In the present Government program for the production of synthetic rubber, the copolymer of butadiene and styrene is the type being manufactures in the largest quantities. It seemed important therefore to make this material, now known as GR–S (Government rubber-styrene type), the next on a research program started some years ago at the National Bureau of Standards to furnish thermodynamic data on various types of rubber, both natural and synthetic, and the monomers from which they are polymerized. Such data have been obtained for unvulcanized natural rubber [1],[1] its monomer, isoprene [2], the equilibrium relationship between the two [3], Hycar OR–15 [4], and 1,3-butadiene [5]. In this paper specific heat measurements on a

[1] Figures in brackets indicate the literature references at the end of this paper.

sample of GR–S synthetic rubber are described, and the increases in entropy, enthalpy, and free energy from 0° to 330° K calculated from them, are included in a table at 5-degree intervals.

II. SAMPLE

The sample of GR-S was especially prepared by J. N. Street, Firestone Tire & Rubber Co., in a laboratory polymerization using a minimum quantity of materials other than butadiene and styrene. The monomers were polymerized in emulsion and coagulated from the latex by the addition of alcohol. An analysis [2] of the material showed that it contained the following:

	Percentage by weight	Estimated standard deviation of method
Carbon	88. 954	0. 018
Hydrogen	10. 2607	. 0036
Ash	0. 37	. 03
Soap as sodium oleate	. 42	. 01
Fatty acid as oleic acid	. 92	. 05
Modifier	. 44	. 05
Phenyl-beta-naphthylamine	. 50	----------
Amount soluble in ethanol-toluene azeotrope	5. 6	. 1

Soap was used as the emulsifying agent, some of which converted to fatty acid. The modifier was added to limit cross linking of the polymer chains, and phenyl-beta-naphthylamine was used as a stabilizer to prevent continued stiffening of the rubber. Ethanol-toluene soluble fractions contain polymer of low molecular weight, in addition to the fatty acid and stabilizer.

The weight percent of styrene units in the polymer was calculated to be 25.50 $\pm$1.26 (the uncertainty assigned is twice the standard deviation). This calculation includes a correction for the carbon and hydrogen in the soap, fatty acid, phenyl-beta-naphthylamine, and modifier.

From the time the sample was received until it was put into the calorimeter for measurements, a period of about a month, it was kept at the temperature of dry ice and in an atmosphere of CO_2 to prevent oxidation or other reactions.

The sample was cut into pieces 10 to 40 mm^3 in volume which were packed between the vanes of the sample container and kept under vacuum for several hours to remove moisture and air. The container was then filled with helium at atmospheric pressure and room temperature and sealed with solder. The weight of the dried sample was 44.920 g corrected to vacuum.

III. CALORIMETER

The calorimeter was of the adiabatic vacuum type described by Southard and Brickwedde [6] (and similar to the one used to determine

[2] Acknowledgment is made to Irving Madorsky and Max Tryon for the analysis of this sample.

the specific heat of natural rubber [1] and of Hycar OR–15 [4]). The apparatus for the measurement of temperature and energy input is described in a paper on butadiene [5].

The sample container used in this particular investigation was made of copper and weighed 80 g, including the platinum resistance thermometer. Eight vertical vanes were included to facilitate heat transfer. The inside surfaces of the container were tinned with Pb-Sn eutectic solder, which was also used for sealing the container.

The heater, of No. 34 constantan wire, fibre glass insulated, was wound on the thermometer case before it was soldered into the reentry tube in the sample container. The heater had a resistance of 50 ohms at room temperature.

IV. DETERMINATION OF SPECIFIC HEAT

The methods of measurement and computation of data were similar to those described in the paper on butadiene [5]. The specific heat, C_p, of the sample was determined by measuring the heat capacity, G_b, of the container plus the sample and then the heat capacity, G_a, of the empty container. The specific heat of the sample is

$$C_p=\frac{G_b-G_a}{M},$$

where M is the mass of sample. A small correction varying from 0.37 percent at 15° to 0.01 percent at 330° K was necessary because of the helium in the filled container.

In order to make a comparison of the different series of observations, a mathematical function was chosen to give close agreement with the data over as wide a temperature range as possible, and deviations of the data from this function were plotted. It was possible when plotting the heat capacity of the empty calorimeter to use the same function (a modified Debye equation) over the entire range from 15° to 330° K. With the heat capacity of the filled calorimeter, however, it was necessary to use several functions over this temperature range. Parabolas have been found to be quite useful particularly at the higher temperatures. The data were usually plotted so that 0.1 percent of G was represented by at least one-half of an inch on the graph except at the lowest temperatures. Although agreement within 0.1 percent of the different runs was considered satisfactory, better results were obtained except below 40°K where the heat capacity is small and in the region just below the transition, as explained later.

Values of the specific heat are given at 5-degree intervals in table 2. The values at 5° and 10° K were calculated from the Debye function, $D(\beta\nu/T)$. The equation used was $C_p=0.03018\ D\ (87.5/T)$, with C_p in joules gram^{-1} degree Kelvin^{-1}. The numerical values were adjusted to obtain good agreement between the equation and the experimental values at 15°, 20°, and 25° K.

It was found that the values of specific heat between −50 ° C and +60° C could be represented within 0.1 percent by the equation

$$C_p=0.4346+7.029\times10^{-4}t+1.156\times10^{-6}t^2,$$

in which C_p is in calories gram^{-1} degree centigrade^{-1}, and the temperature, t, is in degrees centigrade.

V. SECOND-ORDER TRANSITION

This sample of GR-S showed no evidence of the crystallization reported for natural rubber [1], but it exhibited a transition of the second order characterized by a sudden rise of about 40 percent in specific heat. In figure 1 the specific heat curve for GR-S is shown with the specific-heat curves of amorphous natural rubber hydrocarbon [1] and the synthetic rubber Hycar OR-15 [4]. The natural rubber hydrocarbon is a polymer of 2-methyl-1,3-butadine (isoprene), GR-S is a copolymer of 1,3-butadiene and styrene, and Hycar OR-15 is a copolymer of 1,3-butadiene and acrylonitrile. The amount of comonomer (styrene or acrylonitrile) is zero in natural rubber, about 25 weight percent in the GR-S used here, and considerably higher (40 percent or more) in Hycar OR-15. It is to be observed that here the higher amounts of comonomer correspond to the higher transition

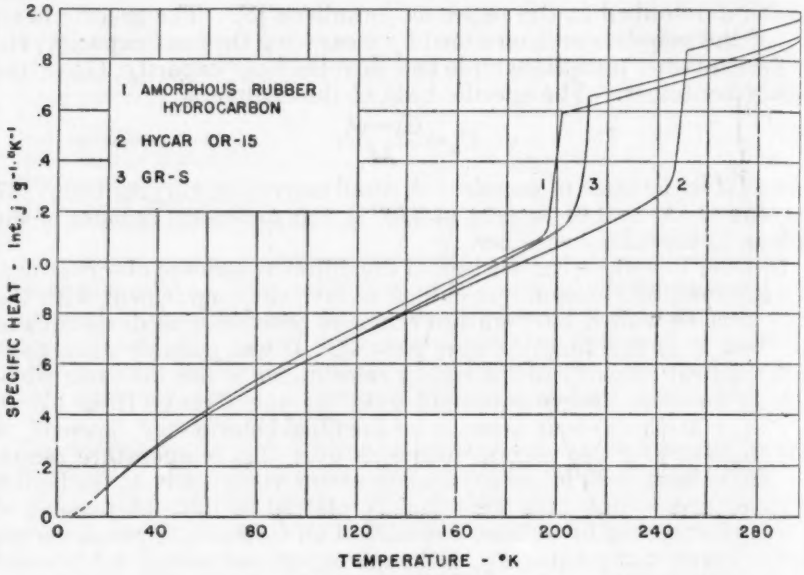

FIGURE 1.—*Specific-heat curves.*

temperatures. Polystyrene has a second-order transition at about 80° C according to Patnode and Scheiber [7].

The experimental data for GR-S indicate that the sharply rising section of the specific heat curve in the transition region intersects the line representing specific heats at higher temperatures, as indicated in figure 1. Although the temperature of the intersection of these two curves is spoken of as the transition temperature, the position of the sharply rising curve is rather uncertain because of wide differences (explained below) between the values of specific heat obtained in the several series of observations in this region. The maximum difference under extreme conditions was 14 percent and the transition temperature varied between −64° and −59° C. Some experimental points at the transition were found to lie above the smooth line representing the specific heat at higher temperatures. This no doubt resulted

from the fact that temperature equilibrium was not realized in the transition region.

In order to get a clearer idea of what was happening in the transition region, a plot of cumulative energy input versus temperature was made for one of the series of observations through this region. With this curve as reference, the other experimental runs were plotted on the same graph, and at least one of the points above the transition from each run was made to fall on the reference curve by shifting the energy-input axis of each. The observations on the upper side of the transition were lined up because it was assumed that the heat content was always the same at any given temperature above the transition temperature. In this graph the transition appears as a slight change

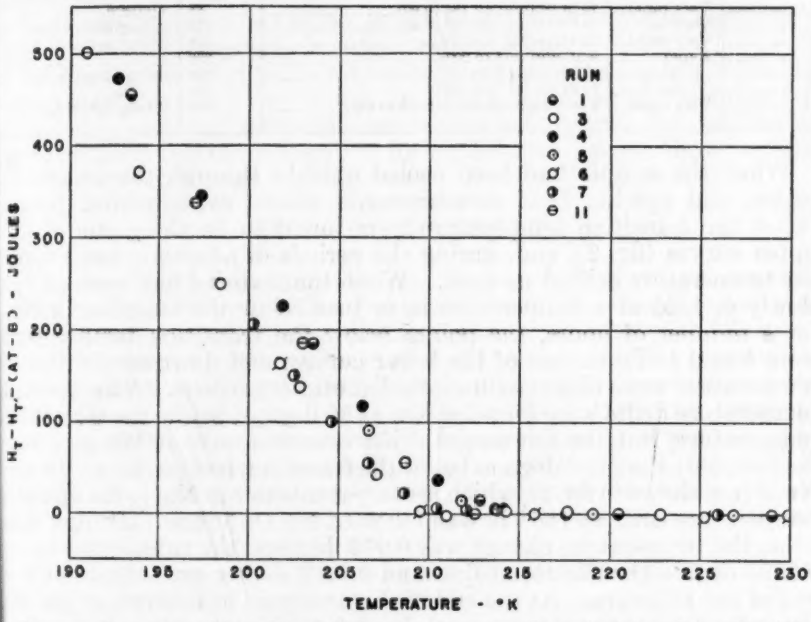

FIGURE 2.—*A sensitive plot of differences between the enthalpies, H, of the filled calorimeter in the transition region for several runs differing in the immediate past history of the sample, i.e. in the length of time the filled calorimeter remained in the transition region.*

Ordinates are differences $H_T - H_{190}° - (103.134T - 22{,}690)$.

in the slope of the curve. In order to magnify this change in slope, a linear equation in T and the total energy added to raise the temperature of the calorimeter was fitted to the region above the transition, and deviations of the experimental data from this equation were plotted versus T, as shown in figure 2.

This plot indicates that the points below the transition are dependent upon the thermal history of the sample between the time it is cooled below and the time it is heated up to the transition temperature. Table 1 gives a record of the thermal treatment before each run and the direction of temperature drifts between heats in the transition region when adiabatic conditions are realized. A "very rapid" rate of cooling indicates that the material was in the transition region

for only several minutes while cooling; a "very slow" rate, that it was in this region for several hours. The starting temperature is the temperature to which the GR-S was heated before heat-capacity measurements were started.

TABLE 1.—*Thermal treatment before runs shown in figure 2*

Run No.	Rate of cooling through transition region	Time held at the given temperature before heating	Starting temperature of specific heat measurements	Temperature drift in transition region
		°K	°K	
1	Very rapid	16 hr—liquid air (85 to 90)	85	*Upward.*
3	Very slow	40 hr—liquid air (85 to 90)	125	Strong *downward.*
4	Very rapid	10 min—(215 to 175)	178	Strong *upward.*
5	Rapid	8–10 min (215 to 200)	200	
6	do	18 hr—solid CO_2 (195)	200	Strong *downward.*
7	do	16 hr—solid CO_2 (195)	200	Do.
11	Very rapid	3 to 4 days—liquid air (85 to 90)	190	Strong *upward.*

When the sample had been cooled quickly through the transition region and specific heat measurements made, experimental points below the transition temperature were found to lie along one of the upper curves (fig. 2), and, during the periods of adiabatic conditions, the temperature drifted upward. When the material had been cooled slowly or held at a temperature in or just below the transition range for a number of hours, the points below the transition temperature were found to lie on one of the lower curves, and downward drifts of temperature were observed under adiabatic conditions. The upward temperature drifts were found as low as 30 degrees below the transition temperature, but the downward drifts occurred only as low as a few degrees, perhaps 6 to 8 degrees below the transition temperature. In run No. 2 (not shown in fig. 2), which is comparable to run No. 1, the upward temperature drift at 186° K was followed for 1½ hours. During this time, the temperature change was 0.075 degrees; the rate of rise being 0.0025 degree per minute at first and 0.0005 degree per minute at the end of the 1½ hours. At the end of the next heat in this run at 196°K, the rate of temperature rise was about 0.003 degree per minute after 7 minutes. After the following heat the rate of rise at 206° was about 0.008 degree per minute after 7 minutes. In all of the observations shown in figure 2, the temperature was measured 7 minutes after the time the heating current was shut off. This is the time ordinarily required for the calorimeter to come to temperature equilibrium.

The observed drifts in temperature and the observed dependence of the specific heat in the transition region on the previous history of the sample are explainable on the basis of a slow approach to a state or condition of lower energy when the sample is in or below the transition region. (See also the paper on Hycar OR–15 [4].) The equilibrium condition evidently changes with the temperature, and the approach to equilibrium becomes slower the lower the temperature, so that at more than a few degrees below the transition region the time required to reach complete equilibrium becomes inordinately long. From this viewpoint the transition temperature depends on the rate of cooling, and at any temperature below the transition the material is essentially in an unstable state. Jenckel [8] studied the second-order transition

of selenium by volume measurements and obtained results which were similar in many ways to observations made.in this investigation. He was able to keep the temperature constant and measure the volume change over the long periods of time necessary to reach equilibrium in the region just below the transition temperature. In a recent paper, Alfrey, Goldfinger, and Mark [10] have studied the second-order transition of polystyrene by volume measurements. They drew many of the same conclusions which had been reached independently in this work from thermal measurements.

From all of these papers it is evident that:

1. The second-order transition temperature depends on the rate of cooling; the faster the cooling, the higher the temperature of transition.

2. If the material is cooled in such a manner that it unedergoes a second-order transition, it is no longer in a stable state.

3. The further the temperature of the material is below thibtransition temperature, the slower is its approach to the equilsi um condition, and at temperatures somewhat below the transsrion temperature, the times required for equilibrium exceed those potiible in ordinary laboratory experiments.

VI. DERIVED VALUES

The increases of entropy $(S-S_0)$ and enthalpy, or heat content, $(H-H_0)$ from 0° to 330° K of this sample of GR–S were calculated by performing tabular integrations of $\int(C_p/T)dT$ and $\int C_p dT$, using Simpson's rule except between 212° and 215°K, where the trapezoidal rule was used. The integrations from 0° to 15° K were calculated from values of specific heat tabulated at 1.25-degree intervals obtained from the Debye equation mentioned previously. The entropy and enthalpy changes from 15° to 200° K and from 215° to 330° K were calculated from values at 5-degree intervals and from 200° to 212° K from values at 1-degree intervals. The results are given at 5-degree intervals in table 2.

The increase in entropy of this sample from the absolute zero of temperature to 25° C is calculated to be

$$S_{298.16}-S_0=1.824 \text{ international joules gram}^{-1} \text{ degree Kelvin}^{-1}$$
$$(\text{or } 0.4359 \text{ calorie gram}^{-1} \text{ degree Kelvin}^{-1}).$$

The increase in free energy $(F-F_0)$ from 0° to 330° K was calculated by the equation

$$F-F_0=(H-H_0)-T(S-S_0),$$

and values at 5-degree intervals are included in table 2.

In accordance with the third law of thermodynamics, the entropy of amorphous GR–S at 0° K is greater than zero. The difference between the entropy of the natural rubber hydrocarbon in its crystalline and amorphous states at 0° K is less than 1 percent of the value of the entropy at 25° C [1]. It is probable that the entropy of random orientation of amorphous GR–S, for each polymerization unit, is of the same order of magnitude as for the natural rubber hydrocarbon. However, the GR–S also has entropy resulting from the randomness of the mixture of butadiene and styrene units, and like natural rubber, randomness of chain lengths.

TABLE 2.—*Specific heat, and increases in entropy, enthalpy, and free energy of GR–S*

[The units of energy and mass are the international joule and the gram, respectively]

T	C_p	$S-S_0$	$H-H_0$	$-(F-F_0)$	T	C_p	$S-S_0$	$H-H_0$	$-(F-F_0)$
°K	$j\,g^{-1}\,°K^{-1}$	$j\,g^{-1}\,°K^{-1}$	$j\,g^{-1}$	$j\,g^{-1}$	°K	$j\,g^{-1}\,°K^{-1}$	$j\,g^{-1}\,°K^{-1}$	$j\,g^{-1}$	$j\,g^{-1}$
0	0	0	0	0	175	.9876	1.0103	91.64	85.16
5	.0036[a]	.0012	.0046	.0015	180	1.0137	1.0385	96.65	90.23
10	.0275[a]	.0095	.0712	.0242	185	1.0394	1.0666	101.78	95.54
15	.0704	.0285	.3124	.1152	190	1.0658	1.0947	107.05	100.94
20	.1127	.0545	.7702	.3195	195	1.0931	1.1227	112.44	106.49
25	.1550	.0842	1.439	.6664	200	1.124	1.1508	117.97	112.19
30	.1958	.1161	2.317	1.166	205	1.182	1.1791	123.71	118.02
35	.2349	.1493	3.395	1.829	210	1.338	1.2092	129.95	124.03
40	.2715	.1830	4.662	2.660	212.3[b]	1.661	1.2248	133.26	126.72
45	.3058	.2170	6.107	3.659	215	1.667	1.2458	137.75	130.05
50	.3380	.2509	7.716	4.829	220	1.678	1.2843	146.11	136.44
55	.3690	.2846	9.477	6.176	225	1.689	1.3221	154.53	142.97
60	.3989	.3180	11.404	7.676	230	1.701	1.3594	163.00	149.66
65	.4277	.3511	13.471	9.350	235	1.713	1.3961	171.54	156.58
70	.4554	.3838	15.679	11.187	240	1.726	1.4323	180.14	163.65
75	.4822	.4161	18.023	13.184	245	1.738	1.4680	188.80	170.86
80	.5091	.4481	20.50	15.348	250	1.752	1.5032	197.52	178.30
85	.5360	.4798	23.11	17.669	255	1.766	1.5381	206.31	185.92
90	.5623	.5112	25.86	20.15	260	1.780	1.5725	215.18	193.65
95	.5879	.5423	28.74	22.78	265	1.794	1.6065	224.11	201.62
100	.6120	.5730	31.74	25.56	270	1.808	1.6402	233.11	209.75
105	.6365	.6035	34.86	28.51	275	1.823	1.6735	242.19	218.01
110	.6612	.6336	38.10	31.60	280	1.838	1.7065	251.35	226.52
115	.6860	.6636	41.47	34.84	285	1.853	1.7391	260.57	235.04
120	.7110	.6933	44.96	38.24	290	1.869	1.7715	269.88	243.84
125	.7363	.7228	48.58	41.77	295	1.884	1.8036	279.26	252.76
130	.7613	.7522	52.32	45.47	298.16	1.894	1.8237	285.24	258.51
135	.7864	.7814	56.19	49.30	300	1.900	1.8354	288.72	261.92
140	.8114	.8105	60.19	53.28	305	1.917	1.8669	298.27	271.10
145	.8364	.8394	64.31	57.40	310	1.933	1.8982	307.89	280.54
150	.8612	.8681	68.55	61.66	315	1.950	1.9293	317.60	290.13
155	.8860	.8968	72.92	66.08	320	1.966	1.9601	327.39	299.83
160	.9109	.9263	77.41	70.64	325	1.983	1.9907	337.26	309.68
165	.9363	.9537	82.03	75.33	330	2.001	2.0211	347.22	319.76
170	.9618	.9820	86.77	80.17					

[a] Calculated from the Debye function.
[b] This temperature was chosen for the transition only for the purpose of calculation.

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DIPOLE MOMENT AND STRUCTURE OF TRIOXANE

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ABSTRACT

Trioxane is a solid polymer of formaldehyde resembling the well-known solvent dioxane in its chemical properties. The molecule can possibly exist in two spacially different forms resembling a chair and a cradle, for which the theoretical dipole moments are 2.3 and 0.6×10^{-18} electrostatic unit (esu), respectively. The experimental value in benzene was found to be 2.18×10^{-18} esu. Hence it is concluded that ordinary trioxane is largely in the chair form, possibly in equilibrium with a small amount of the cradle form. This cyclic ether would therefore be suitable for mixing with nonpolar solvents to study the effect of increased polarity on the activities and absorption spectra of indicators.

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I. INTRODUCTION

Trioxane, frequently called α-trioxymethylene, is a cyclic trimer of formaldehyde. Its physical and chemical properties have been discussed by Walker and Carlisle [1].[1] Studies of Raman spectra [2] and crystal structure [3] indicate that it has a puckered, six-membered ring structure analogous to that of cyclohexane. Consequently, it may exist in two stereo isomeric forms, as discussed by Sachse [4] and by Mohr [5]. They are usually designated as the "chair," or Z, and the "cradle," or C forms.

Until recently the structure of cyclohexane and other six-membered monocyclic compounds was open to doubt. Chemical evidence based upon the Thorpe-Ingold hypothesis of valency deflection [6] indicated considerable strain in the cyclohexane ring and suggested a planar structure. On the other hand, the Sachse-Mohr theory of strainless rings required that these cyclic compounds have a puckered or multiplanar configuration and may exist in at least two isomeric forms. The isolation of two stable forms of decahydronaphthalene [7] corresponding to the "chair" and "cradle" structures confirmed the Sachse-Mohr theory for bicyclic compounds. Since then such isomerism has been demonstrated in a number of other bicyclic and polycyclic compounds. However, despite numerous attempts to isolate two such forms of cyclohexane derivatives and other mono-

[1] Figures in brackets indicate the literature references at the end of this article.

cyclic compounds, there is no authentic proof of the separate existence of any such isomeric forms. Apparently, the strain of valency angles involved in passing from one of the strainless forms to the other is not sufficiently great to prevent rapid conversion of one to the other. Stability of the two isomers of decahydronaphthalene is supplied by the interlocking ring system, which prevents change of the two forms into each other without rupture of a covalent bond. One might expect that under ordinary conditions many six-membered monocyclic compounds would exist as equilibrium mixtures of the "chair" and "cradle" forms. It appears, however, that such a mixture containing appreciable amounts of both forms has been established only in the case of cyclohexane-1,4-dione.

The dipole moment of this compound in benzene solution has been found to be 1.3 D[2] [8]. This value is intermediate between that calculated for the "chair" ($\mu=0$) and the "cradle" ($\mu=3.9$ D) forms and corresponds to an equilibrium mixture containing about 10 percent of the "cradle" form. In the case of heterocyclic compounds, such as dioxane, paraldehyde, and morpholine, as well as cyclohexane and its derivatives, definite evidence for the existence of the "chair" form alone has been obtained. The isolation of two forms of methylcyclohexane corresponding to the two possible multiplanar structures has been claimed recently [9] but conclusive proof is lacking.

To determine whether the "chair" or the "cradle" form is the stable one in solution at ordinary temperatures or whether the solution consists of an equilibrium mixture of the two forms, the dipole moment of trioxane has been measured using benzene as solvent. With trioxane, the "chair" form would have a fairly large dipole moment, whereas the "cradle" structure would have only a small moment. The experimental data give a dipole moment of 2.18 D for trioxane.

II. EXPERIMENTAL METHODS AND RESULTS

Trioxane obtained from E. I. du Pont de Nemours & Co. Inc., was recrystallized from cyclohexane and then sublimed. The melting point was 61° C. The benzene, of analytical grade, was distilled immediately before use.

A heterodyne beat method was used for the measurement of the dielectric constants. The cell was a specially designed glass vessel with silver-mirror surfaces to serve as plates. Measurements were made in an air bath regulated at 30°±0.02° C.

The experimental data are listed in table 1. The molar polarization of the solute at infinite dilution, P_2^∞, is calculated from the Hedestrand equation [10],

$$P_2^\infty=\frac{3P_1}{(\epsilon_1-1)(\epsilon_1+2)}\frac{\Delta\epsilon}{f_2}-\frac{P_1}{d_1}\frac{\Delta d}{f_2}+P_1\frac{M_2}{M_1}.$$

Wherever used, the subscripts 1, 2, and 12 refer to the pure solvent, solute, and solution, respectively, f expresses the concentration in mole fraction, ϵ represents the dielectric constant, d is the density, and M is the molecular weight. $\Delta\epsilon$ equals $\epsilon_{12}-\epsilon_1$, and Δd equals $d_{12}-d_1$. P_1, the molar polarization of the solvent, is defined as

[2] D (Debye) $=10^{-18}$ esu.

$$\frac{\epsilon_1-1}{\epsilon_1+2}\frac{M_1}{d_1}.$$

The above equation reduces to

$$P_2^{\infty}=14.86\frac{\Delta\epsilon}{f_2}-30.67\frac{\Delta d}{f_2}+0.3412\ M_2$$

when the numerical values for the constants of the solvent are inserted. The dielectric constant and density of pure benzene at 30° C were taken as 2.2627 and 0.8684, respectively. P_E is the electronic polarization obtained by summation of the atomic refractivities listed in Landolt-Bornstein Tabellen. The dipole moment was calculated from the relation

$$\mu=0.223\ (P_2^{\infty}-P_E)^{\frac{1}{2}}\times10^{-18}\ \text{esu.}$$

TABLE 1.—*Mole fraction, f_2, increment of dielectric constant, $\Delta\epsilon$, and dipole moment, μ, of trioxane*

f_2	$\Delta\epsilon$
0.00448	0.0276
.01083	.0671
.01695	.1054
.02155	.1342
.02443	.1516
$\Delta\epsilon/f_2=6.20$	
$\Delta d/f_2=0.283$	
$P_2^{\infty}=114.4$	
$P_E=18.8$	
$\mu=2.18\times10^{-18}$ esu.	

III. DISCUSSION

The two possible isomeric structures for trioxane are illustrated in figure 1. The "chair" form has an axis of symmetry perpendicular to the plane of the three carbon atoms. The three oxygen atoms lie in a plane parallel to and slightly below this plane. Calculation of the dipole moment of the "chair" form by vector addition of the bond moments gives 2.3 *D* if the C—O and C—H bond moments are taken as 0.9 *D* and 0.2 *D*, respectively, and all of the valence angles are assumed to be tetrahedral. The moment calculated for the "cradle" form is 0.6 *D*. In view of the necessarily rather approximate nature of the calculated moment, the agreement between the actual value of 2.18 *D* and that calculated for the "chair" form is as good as could be expected. The presence of a small amount of the practically nonpolar "cradle" form, however, is not excluded.

Trioxane is closely related structurally to the more familiar paraldehyde, which is a cyclic trimer of acetaldehyde containing alternate carbon and oxygen atoms in the ring and differing from trioxane only in that one hydrogen of each methylene group has been replaced by a methyl group. Unlike trioxane, however, which has only one possible structure for each of the two Sachse-Mohr forms, paraldehyde has four possible stereoisomeric structures for the "chair" and for the "cradle" configurations. Electron diffraction studies [11] of paraldehyde vapor are in favor of a "chair" structure, in which the

three methyl groups are symmetrically located in a plane parallel to and close to the plane formed by the three carbon atoms of the ring, and in which all the valence angles are approximately tetrahedral. The dipole moment of paraldehyde has been found to be 2.03 *D* [12] in benzene solution. Although this value is somewhat lower than that found for trioxane, whereas a slightly higher value might be expected because of induction effects in the methyl groups, it does lend support to a "chair" structure for the molecule.

The cyclic ether, trioxane, in the molten state or mixed in various proportions with other solvents, would have very useful solvent properties somewhat similar to those of dioxane. It can be dissolved in varying amounts in nonpolar solvents to increase polarity, and in this connection should prove of interest in investigations on the effect of various polar and nonpolar organic compounds and solvents on the absorption spectra of indicators and their changes by organic acids and bases.

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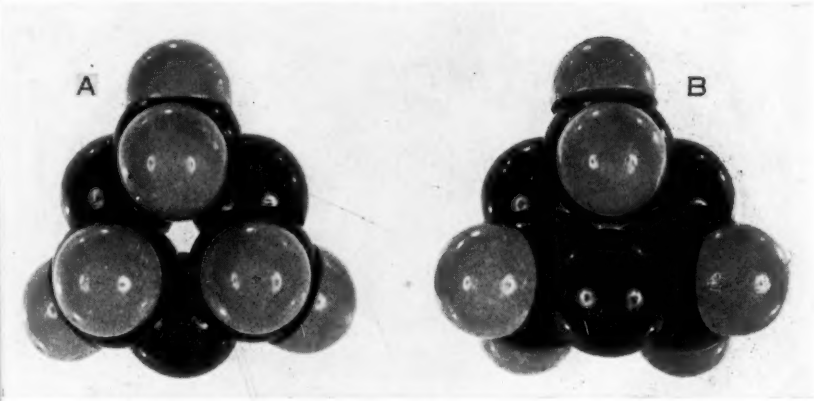

FIGURE 1.—*Chair (A) and cradle (B) configurations of trioxane.*

Two hydrogens (light colored atom models) are attached to each carbon (black models). The other atom models are the oxygens connecting the carbons.

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